THE OIL SHALES OF TASMANIA

AND

NEW SOUTH WALES.

PREFACE.

as required by D.Sc. Regulations, Paragraph 2.

The accompanying volume comprises a series of ten papers, bound for convenience in handling, which are the collected results of an investigation into the nature, treatment, and character of the distillation products, of Tasmanite Oil Shale and of certain New South Wales Oil Shales carried out during the six years 1928-1933 in the joint laboratories of the chemistry departments of the University of Tasmania and of the Hobart Technical College and under the control of the Engineering Board of Management.

The papers are bound in the following order, which is, with some exception, that in which the investigation was carried out.

1. Behaviour of Tasmanite Oil Shale on heat treatment under constant volume conditions.
2. Further study of the pyrolysis of the oil producing material in Tasmanite.
3. General investigation of Tasmanite Oil Shale retorting.
4. Distribution of sulphur in the standard sample of shale.
5. Nature and composition of the oil yielding materials of Tasmanite.
6. Tasmanite Shale Oil.
7. Composition of Tasmanite shale oil distillates.
8. General Review of Tasmanian shale position, September 1933.
9. Comparative work on New South Wales Oil Shales.
10. New South Wales shale oils.

Owing to the unexploited nature of this field of enquiry, the work is practically entirely of an original character and little direct assistance could be gained from the literature. In addition, the thousands of assays, determinations, etc. were all personally carried out by the writer, prolonging the work in point of time but maintaining a uniform standard of accuracy. The only substantial assistance was on the mechanical side in the construction of apparatus. The actual designing of the special apparatus used was done by the writer, so that almost the whole of the work may be looked on as original and in the few instances where other sources of information have been used they have been duly noted.

No part of this work has been previously submitted for any degree and little has been published as the work was commenced under the old regulations for the degree of D.Sc. and these demanded a thesis not previously published. When the regulations for the degree of D.Sc. were recently altered, the work had proceeded to such a stage that it was thought advisable to leave the collection and presentation of it till all the laboratory work had been completed.

The provision of some special apparatus was made by assistance from the Council of Scientific and Industrial Research, through the Commonwealth Science and Industry Endowment Fund. The results of the investigation, although not published except in a partial and fragmentary form in the "Report of Tasmanian Shale Oil Investigation Committee", Government Printer, Hobart, 1933, have been freely made available to both Commonwealth and State Governments and the stage which the investigation had reached in 1931 enabled the Investigation Committee to proceed immediately to a proper evaluation of the shale resources of Tasmania. The comparative work done on the New South Wales shales and their resultant oils has been made use of by the Newnes Investigation Committee in their deliberations at the close of 1933.

THE OIL SHALES OF TASMANIA

AND

NEW SOUTH WALES.

A Monograph embodying the results of an investigation carried out during the years 1928 to 1933 in the joint laboratories of the University of Tasmania and Hobart Technical College and under the control of the Engineering Board of Management. The subject of investigation was the Tasmanite oil shale of the Mersey valley, Tasmania, and its distillation products. Comparative work on the oil shales of the Hartley Vale, Capertee Valley, and Newnes areas in New South Wales has been carried out and is also included.

INTRODUCTION.

It has become increasingly evident during the last few years that the attempts to extract oil and produce refined petroleum products from the Tasmanite oil shale have not been as successful as could be desired. This, in the writer's opinion, has been partly or principally due to a lack of knowledge of the shale itself in particular, of shale retorting generally, and of the nature of the Tasmanite shale oil and its distillation products.

In view of the need for research on the Tasmanite oil shale, work was commenced in 1928 on a fairly extensive programme and continued through the years 1929 to 1933, inclusive. The chief feature of the work to be regretted is the undue prolongation of the investigation necessitated by the limited time available in each year owing to the pressure of academic and other duties.

However, it is felt that a considerable part of the work done is of interest to those technologists interested in the local shale industry and, while some parallel work has come to light from other countries since the investigation was well in hand, the results of this work have direct application to the shale oil industry in Tasmania and on this account have a particular and definite value. As to exactly how much of the work carried out should be given the writer is in some doubt, but the detail which is given may prove in unexpected ways to be useful to those interested.

During the course of the retorting investigation it has developed that successful retorting of the Tasmanite shale is mainly an engineering problem. The conditions necessary for successful retorting can be fairly well gleaned from the literature on oil shale and the writer's work on the retorting of Tasmanite shale has confirmed the general results obtained in other countries and established that Tasmanite is no unique type, but merely representative of a particular class of shales (Ichthyol schists:) found in many lands, while the New South Wales shales are representative of an entirely different class. It has been possible to examine some New South Wales shales from the Newnes, Hartley Vale, and Capertee Valley areas for comparative purposes and, in general, the principal differences are that Tasmanite yields an asphaltic base oil high in sulphur, while the New South Wales shale yields a paraffin base oil comparatively low in sulphur. The oil content of the New South Wales shales is also considerably higher, averaging about three or four times the yield of Tasmanite.

The whole of the experimental work of this investigation was carried out in the joint chemical laboratories of the University of Tasmania and the Hobart Technical College and administered by the Engineering Board of Management, to whom due acknowledgement is made

of the use of rooms and equipment. The thanks of the writer are also due to the Council of Scientific and Industrial Research for financial assistance for the purchase of unusual and special apparatus, and also indirectly to the Council for the stimulus given by the offer of such assistance. Timely assistance has also been given by the Council in order to complete the collection of the results and the gathering together into a finished form.

My personal thanks are also due to many others for assistance and co-operation. To Mr. Anderson, late manager of the Tasmanite Shale Oil Company, for many samples of oil and shale, to Mr. A. Walker, B.Sc. of Mineral Oils Extraction Ltd. for samples of oil and shale and for inspiration gained by discussion of Tasmanite shale problems. Mr. W. H. Schneider, B.E., B.Com., Lecturer in Mechanical Engineering, University of Tasmania, gave timely assistance in gauge calibration and other ways. Mr. V. V. Hickman, B.A., B.Sc., Ralston Lecturer in Biology, University of Tasmania, prepared the slides and microphotographs shown in section V. Mr. C. Law of the Hobart Technical College has given much assistance on the mechanical side by suitable advice and by the making of many parts. Mr. S. M. Seares has prepared many of the sketches, but in justice to his skill I should add that the graphs were drawn by myself.

On the whole it is regretted that so much time has elapsed before publication of the results, but they are now submitted as a record of work done and it is hoped that a valuable contribution to the knowledge of Tasmanite oil shale has been made, and that future investigators may find herein a trustworthy foundation on which to build.

E. E. Kurth

Hobart. December 1933

CORRECTION.

Line 2. "Council of Scientific and Industrial Research" should more correctly read "Trustees of Commonwealth Science and Industry Endowment Fund".

Lines 4 and 5. "Council" should read "Trustees".

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PART IX. Continued.

PART I

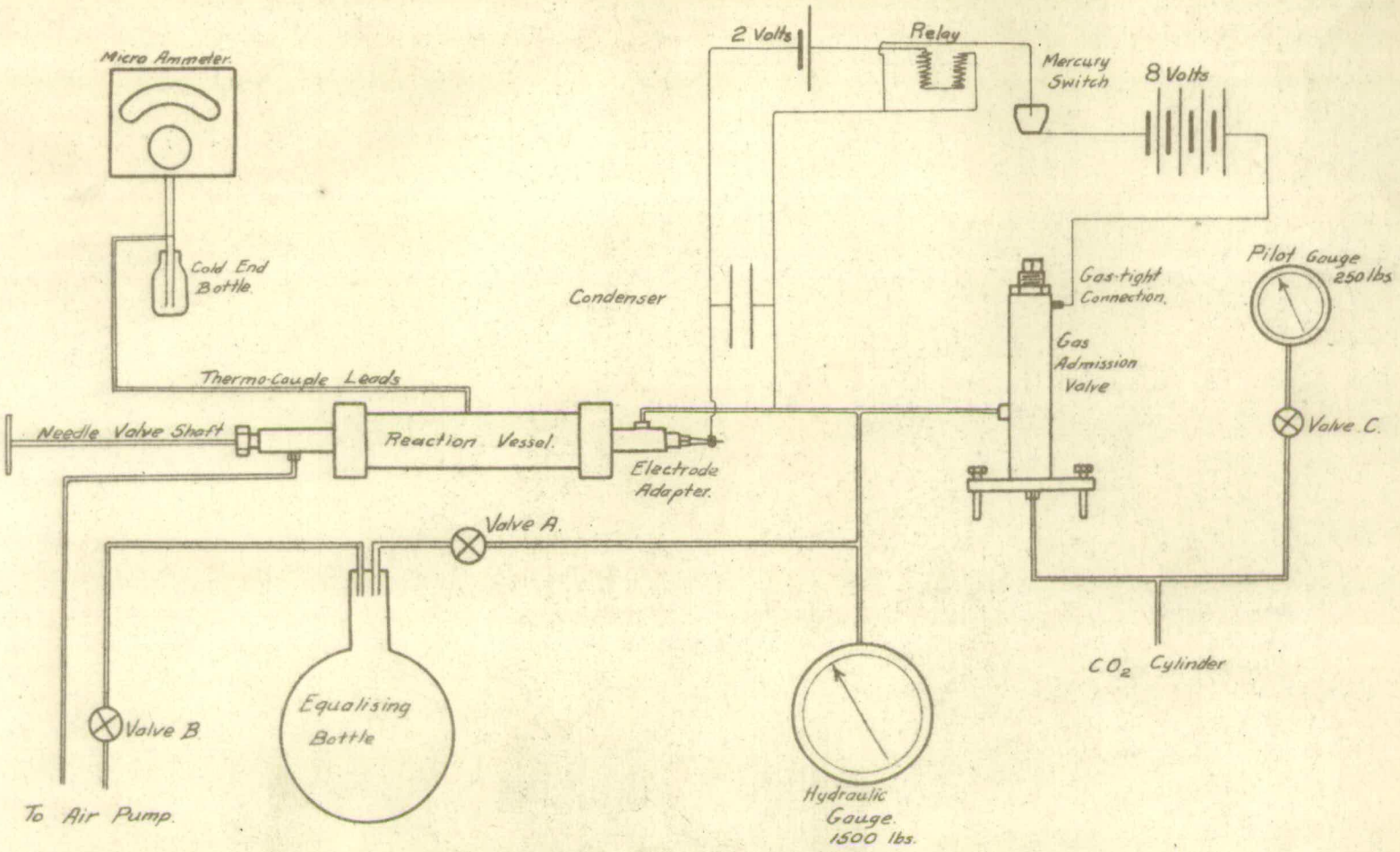
BEHAVIOUR OF TASMANITE OIL SHALE ON HEAT TREATMENT UNDER CONSTANT VOLUME CONDITIONS

The first portion of experimental work carried out was an investigation of the decomposition of the organic matter in the shale by observation of the vapour pressure of gaseous and volatile products over a period of slow heating in a specially designed and constructed constant volume reaction vessel of suitable strength to withstand the pressures experienced.

The apparatus would have been much simpler to construct and operate if a direct connected pressure gauge could have been used for measuring the pressures. The condensation of oil in the connecting pipes made this simple form of apparatus quite impossible so that means had to be devised to measure the pressure without contaminating or withdrawing the contents of the reaction vessel.

This, in general was attained by having a diaphragm within the reaction vessel on one side of which the pressure of the contents of the vessel operated while on the other side of the diaphragm carbon dioxide under pressure balanced that of the gases and vapours. Increase of pressure within the vessel closed an electric circuit operating through a relay an electrically controlled gas admission valve which admitted the necessary amount of gas to open the circuits again. The balancing gas was thus admitted automatically to keep up in pressure with the rising pressure in the vessel. By leaking away very slowly the carbon dioxide a falling pressure could be just as easily followed. The advantage of the apparatus was that the pressure in the vessel could be read at any reasonable distance from the vessel by an ordinary hydraulic pressure gauge of suitable range. Owing to an unfortunate variable change in the zero of the Australian made gauge used very accurate measurements of the pressure were precluded in spite of the fact that the gauge was subsequently recalibrated by a dead weight gauge testing apparatus.

The diaphragm operating pressure for a robust diaphragm was less than 5 cm. of mercury or 1 lb. per square inch and provided it was not strained this sensitivity was retained. More sensitive diaphragms were made but owing to the uncertainty of the readings of the pressure gauge to 2 or 3 lbs the more robust type of diaphragm was adopted.



GENERAL ARRANGEMENT OF APPARATUS

Scale 1/8 approx.

The general arrangement of the apparatus used is shown in the accompanying print.

The reaction vessel was of cylindrical form 12 inches by 1½ inches internal dimensions and thick walled to provide ample strength at red heat and to facilitate heat distribution. It was formed by boring 2½"steel shafting so as to leave ½" thickness walls. The ends were screwed on the outside 12 threads per inch for a length of 1½ inches approximately. The ends were turned true and scraped where necessary to a plane surface.

The end caps were made of 3½ inch steel shafting bored out to a depth of one inch. The length of each cap was 1½ inches so that all thicknesses were ½ inch. The caps were screwed to fit the barrel. A permanent gasket was formed by brazing in each cap an annular ring of 1/8 inch sheet copper, 2½" outside diameter and 1½" internal diameter which was faced as true as possible and scraped to accurately fit the plane end of the barrel. The choice of the copper gasket was made on account of its greater thermal expansion so that with elevated temperature it would give a tighter joint. Provided that it was smeared before screwing up with jeweller's rouge made into a paste with eucalyptus oil, the joint remained perfectly gastight even on raising the temperature to 600 C. Carbonisation of some of the oil no doubt helped to seal the joint.

Into one end cap and ½" from the centre was fitted a needle valve which allowed the air to be exhausted through a ¼" copper tube at the beginning of a run and after a run served as an outlet through which gas could be released and oil distilled. The valve stem was 12 inches long enabling the valve to be operated while the vessel was in position in the furnace.

The other cap carried centrally the diaphragm and insulated electrode. The diaphragm itself was carried on a specially designed screwed plug which screwed from the inside through the end wall of the cap leaving a threaded projection on which to screw the adaptor which again carried the sparking plug with its central electrode extended by a small iron tubular section ending in a platinum contact. The screwed plug was bored with a ¼" hole for the electrode and the inside end was extended as a spigot for 5/32 inch. A steel washer 15/16" diameter and 1/8" thick with ½" hole was slipped on then also a 1½" diameter 22 gauge nickel disc with ½" hole. The periphery of the disc was ground thin and turned up at right angles ready to receive the diaphragm. The nickel disc was then attached to the screwed plug with silver solder, 75 silver 25 copper, brought up to a free flowing heat with a gas blow pipe.

Metal for the diaphragm was not easy to find at first but some extra pure soft nickel sheet from May and Baker, Battersea, London rolled out to .005" possessed the sought for mechanical

property of retaining its elasticity after repeated heatings to 1000 C as encountered in the soldering processes. Platinum, gold, and silver all became so very soft as to be useless. The nickel proved comparatively inert as regards attack by sulphur compounds and so proved chemically suitable also. The sample of nickel used could be rolled down to .001" with ease but this degree of thinness was unnecessary.

The attachment of the central contact proved also a difficulty as a high melting solder had to be used to fix the contact to the diaphragm and still allow the diaphragm to be soldered to its receiving disc with silver solder sufficiently high melting as to retain its strength at 600C. A platinum contact soldered with pure silver to the nickel cracked the nickel at the point of attachment and a pure gold contact disc 5/32" diameter was substituted. By attaching the gold contact at its centre only the results of differences of expansion were minimised.

The method of attachment found satisfactory was to melt about 1/10 milligram of borax glass on the nickel diaphragm at the desired point, then place thereon a ½ to 1 milligram bead of pure silver and heat to the melting point of silver to attach the silver to the nickel. The gold contact was then placed in position and the whole raised to the melting point of silver again when a slight subsidence of the gold indicating the melting of the silver and its alloying with the gold took place. No silver would be visible at the edge of the gold disc. Contacts fixed in this way proved perfectly satisfactory.

The prepared diaphragm was then fitted into the nickel disc with its upturned edge and the edge gently hammered down to hold the diaphragm. The joint was then completed by silver soldering avoiding the spreading of the solder inwards by using too much borax and at the same time keeping the flame away from the centre of the diaphragm carrying the gold contact.

The elongated electrode of the sparking plug carried a platinum contact which was kept short so that the expansion of the steel electrode adaptor would be practically completely compensated by the expansion of the electrode extension.

The sparking plug provided an efficient way of carrying an insulated connection through to the diaphragm at pressures up to 60 atmospheres. There was slight leakage of gas between the central electrode and the insulator but as this only represented waste of carbon dioxide this was not serious, the actual measurement of pressure not being interfered with. The sparking at the diaphragm contact was minimised by having a condenser of suitable capacity across the break and the relay operating current of 30 to 40 milliamperes gave no trouble with contact burning under these conditions.

The electrically operated gas admission valve was constructed as follows. A triangular piece of ½" steel plate served as a base and at each apex a 2½" by 3/8 steel stud served the double purpose of giving room underneath for a gas connection and providing a means of levelling. Into the centre of the plate a fairly substantial brass block was screwed. This block served as the means of attachment of the solenoid tube and carried on its lower side a gas connection in the shape of a petrol union and on its upper surface the seat for the needle valve.

The solenoid tube was of annealed soft steel 8½" long and 1¾" external diameter. The internal diameter was 1¼ inches. The joint with the brass valve seat block and the base plate was rendered gastight with boiled oil and red lead.

The solenoid bobbin was made by tightly fitting on to a ¾" core of annealed soft steel 3/16" thickness end discs. The upper one was of steel and threaded to screw in the upper end of the solenoid tube. The lower one was of brass and a sliding fit in the tube. A slot provided in the upper bobbin end allowed the vertical position of the bobbin to be varied by screwing up or down before completing the electrical connection.

The core of the bobbin was bored with a ¼" hole through which passed the ¼" brass valve stem just a sliding fit.

The valve stem was threaded at each end and on the upper end carried two thin brass nuts of ¾" diameter on the upper one of which the valve loading spring pressed.

The screwed plug serving to seal the upper end of the solenoid tube was recessed to give a seating for the loading spring and vertical adjustment of this plug applied the necessary loading to the valve stem. When the correct position of the plug had been found by trial a ¼" thickness lock nut was screwed on and sweated in position with soft solder. The joint with the solenoid tube was rendered gastight by screwing in the hot plug coated with fairly hard bitumen.

The lower end of the valve stem carried a 3/16" thickness and 1¼" diameter iron washer or circular nut locked in place by a brass nut.

It was thus possible by the various adjustments to vary the lift of the valve and load the control spring so as to secure any desired rapidity of return of the valve when the circuit was broken.

The bobbin was wound with seven layers of 22 gauge double cotton covered wire giving a resistance of approximately 2 ohms. One end of the wire was earthed on the brass bobbin end and the other end carried through the steel bobbin end then through the solenoid tube wall by means of a small petrol union. A hard sealing wax served the dual purpose of insulator and gas seal

Provided that the joint was screwed up at a temperature of about 150 C the joint gave no trouble with gas leakage at pressures up to 60 atmospheres.

The current necessary for operation of the valve with the greatest loading of the control spring found necessary was four amperes. Four storage cells thus provided ample current and this was broken at a mercury break operated by the diaphragm circuit.

A petrol union screwed into the wall of the solenoid tube just above the valve seat was provided for the gas connection to the diaphragm chamber.

The essential details of construction of the reaction vessel and gas admission valve are shown in the accompanying sectional sketch drawings.

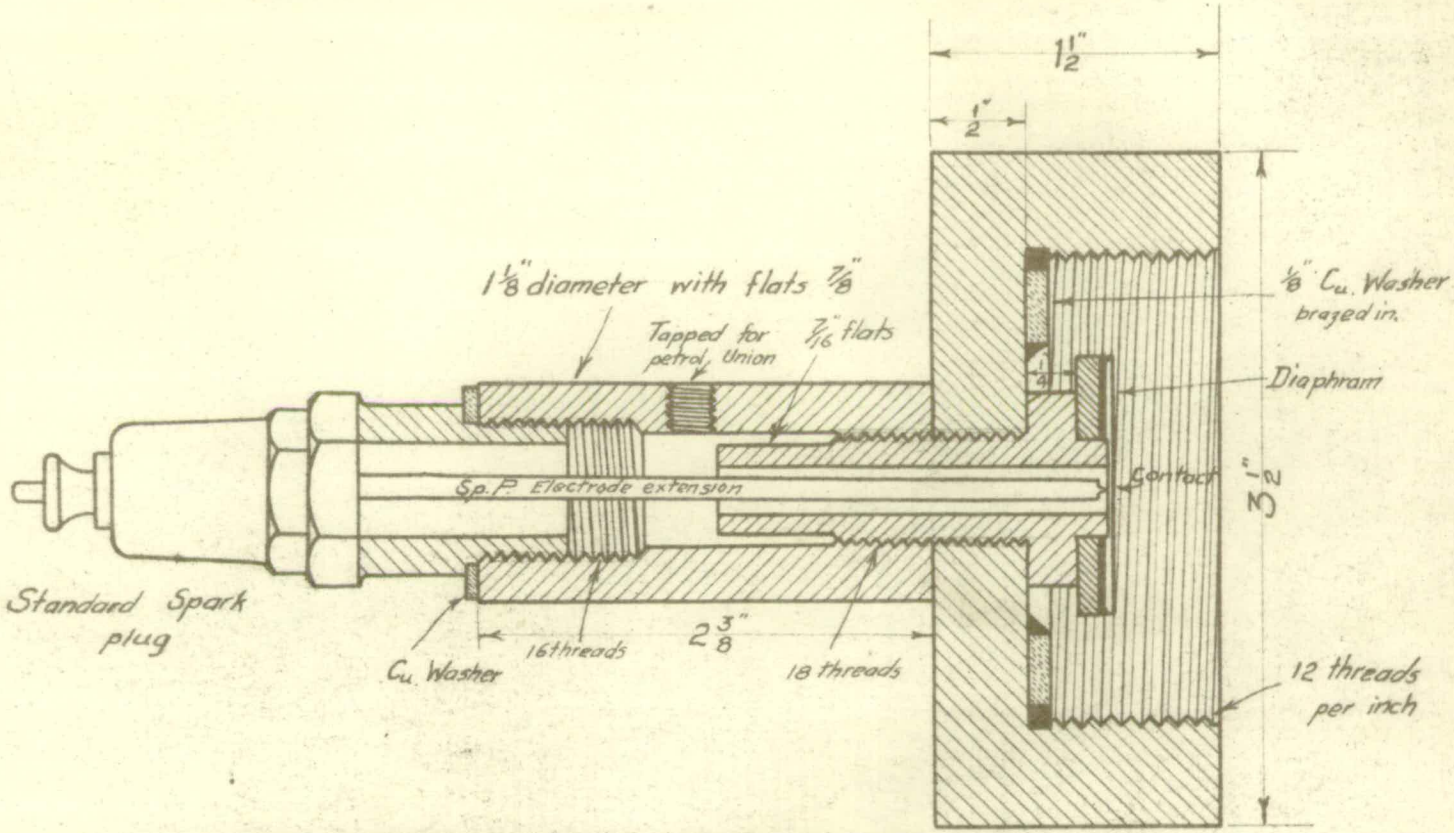
All gas connections were made with 1/8" outside diameter solid drawn copper tubing as used for petrol lighting sets as this tubing is of ample strength and after annealing at red heat can be bent and manipulated like ordinary copper wire. The usual unions used on this tubing proved very convenient and gastight at pressures up to 100 atmospheres and over. For attachment to the tubing silver solder was used. For the connection to the diaphragm chamber a specially made nut of larger dimensions to allow for the weakening of the brass at red heat was found necessary.

The heating furnace was of tubular form 24 inches long and 4 inches internal diameter and wound with three separate windings of 26 gauge nichrome wire as in a triple thread. Two of these were in parallel for quick heating and for general work with this apparatus one only was used giving a temperature rise of one degree Centigrade per minute at 400 C to 450 C. Magnesia boiler lagging proved very suitable as a heat insulator for covering the windings and a bright tin sheet further conserved heat and gave more uniform temperature conditions. In order to maintain a more uniform temperature in the furnace the windings were more closely spaced toward the ends than at the centre.

The wall temperature of the reaction vessel was taken by means of an iron-constantan thermocouple the junction of which was inserted into a shallow 1/8" hole and pened in. A thermos flask was used as a constant temperature cold end and a 636 ohm Cambridge L pattern microammeter as indicating instrument. Temperatures could be read to 1 degree C with care. The temperature- E.M.F. curve of the couples used were drawn from observations at five points. These were boiling water, freezing tin, lead, and zinc, and boiling sulphur.

The construction of the various parts of the apparatus was executed from my design by R. L. Ditcham, General Engineering Works, Hobart and the accuracy of the joint surfaces was very satisfactory indeed, making possible the working of the apparatus at high pressures and over a considerable range of temperature when the correct jointing materials and gaskets had been found.

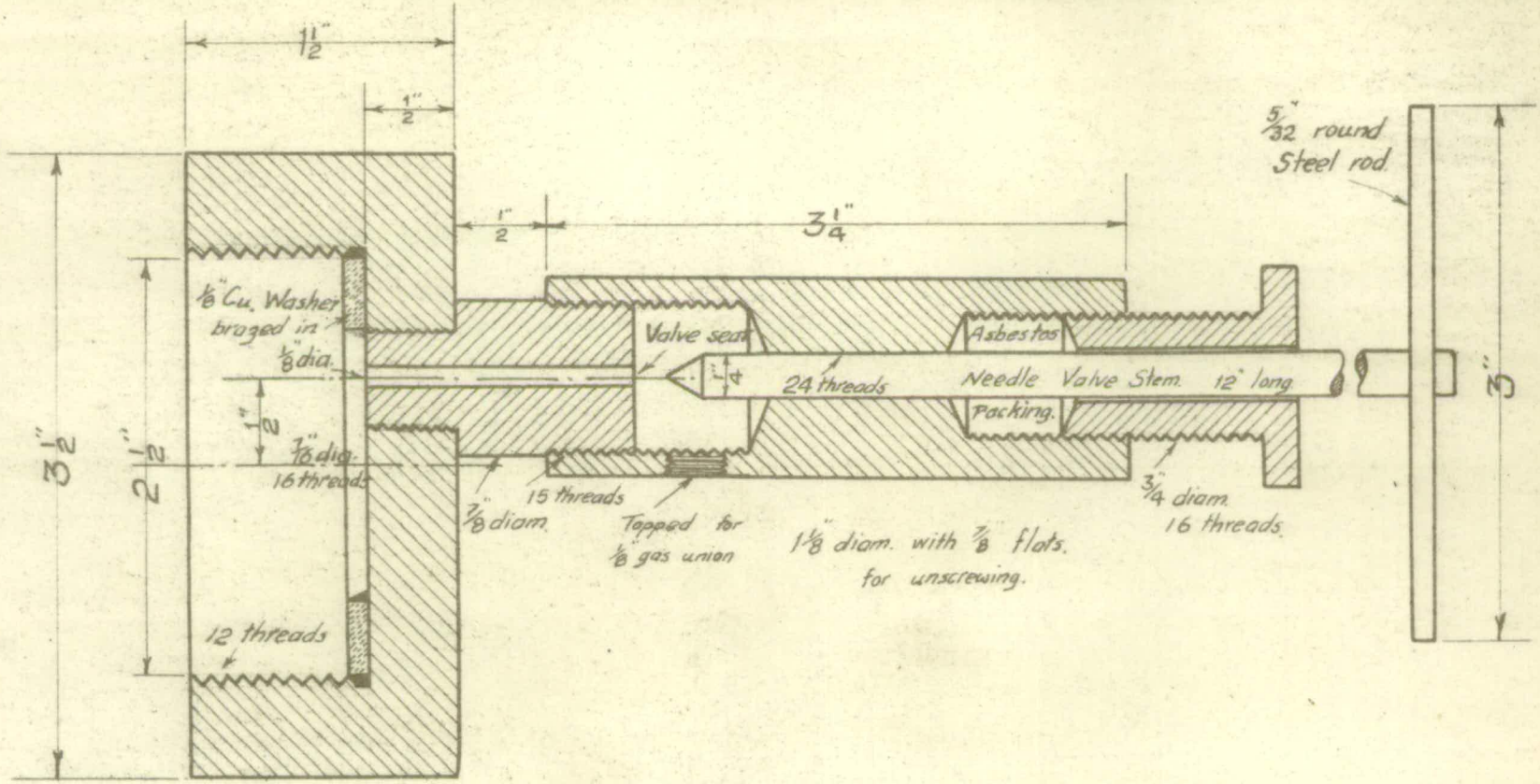
REACTION VESSEL DETAILS



SECTION DIAPHRAGM CAP ASSEMBLY

Full Size.

REACTION VESSEL DETAILS

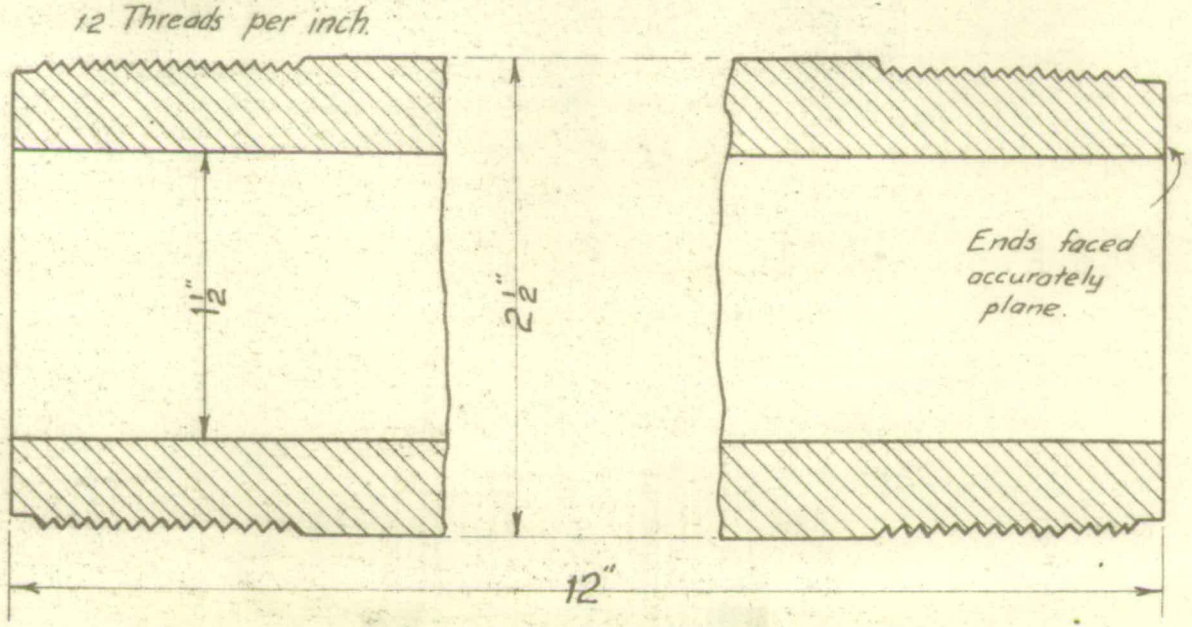


SECTION NEEDLE VALVE CAP

ASSEMBLY

Full Size.

Reaction Vessel Details.



Section of Barrel

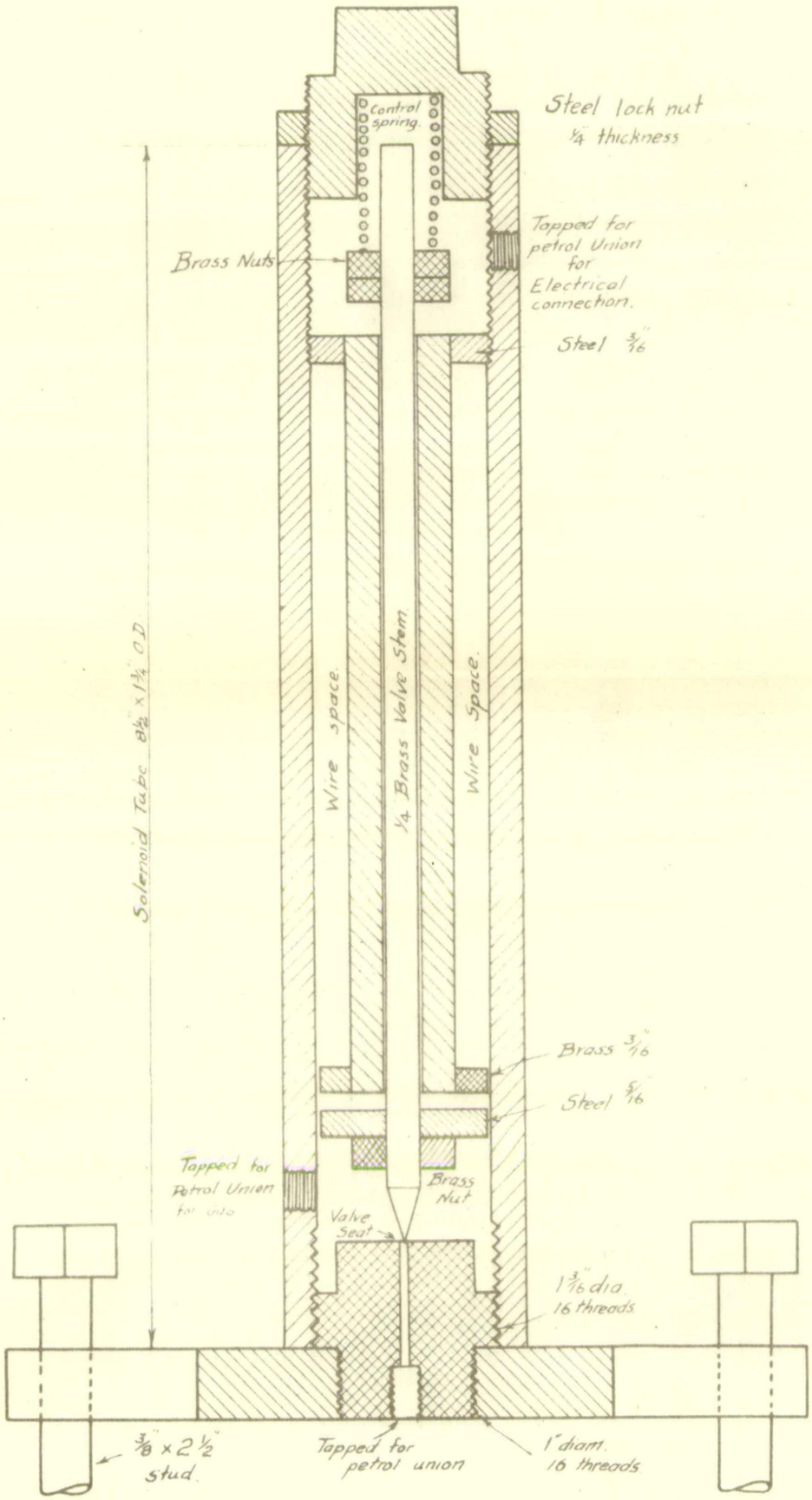
Full Size

SECTION OF GAS ADMISSION VALVE

SHOWING PRINCIPAL DETAILS

Full size.

Solenoid Tube
8½" x 1¾ O.D.



METHOD OF USING APPARATUS

According to the richness of the shale, 50, 100, or 150 grams of shale dried to constant weight at 100 C were placed in the vessel, the joint faces smeared with rouge and eucalyptus oil and the end caps screwed on as tightly as possible. The copper pipe connection to the needle valve chamber was then made.

The vessel was then placed in the heating furnace, the gas connection to the diaphragm chamber made, and the power switched on. Valves A and B were then opened, the valve on the carbon dioxide cylinder tightly shut, and with the needle valve open the air exhausted from both the inside of the reaction vessel and from the whole of the gas system. This was not usually done till the temperature of the vessel exceeded 100 C so that any surface moisture would be removed. An ordinary mercury U-tube manometer was used at this stage in place of the hydraulic gauge which was arranged so as to be readily connected in a second or two when required.

When the manometer showed a pressure of about 30 m.m. only the needle valve was shut thus sealing the bomb or vessel. Valve B was then shut and provided no leaks were showing the apparatus was ready for the run.

When the pressure in the vessel began to rise the diaphragm would be displaced sufficiently to close the contact and through the relay to close the mercury switch thus lifting the needle of the gas admission valve and allowing gas to flow into the diaphragm chamber. Adjustment of the pressure on the gas cylinder side of the admission valve was necessary so as to avoid too great a gas flow in the early stages of a run. This was secured by having a 250 lbs. pilot gauge to indicate this pressure. When the pressure necessary exceeded the range of the gauge the valve C was shut and the gauge union slackened for safety.

It was also found convenient owing to the small volume of the carbon dioxide system to include an equalising vessel of 3 litres capacity between the valves A and B to allow of more accurately following the rise of pressure in the early stages of the heating. When atmospheric pressure was reached in the reaction vessel, valve A was shut cutting out the equalising flask and at the same time the measurement of the pressure was transferred from the mercury manometer to the hydraulic gauge.

The usual practice during a run was not to allow the valve on the carbon dioxide cylinder to remain open until after the pressure in the gas system reached about 30 atmospheres. The slight leakage past the gas admission valve made it desirable to keep the pressure on the cylinder side of the valve within 200 lbs or so of the pressure in the gas system. The increasing frequency of operation of the gas admission valve which made a distinctly audible click on shutting would call attention to the need of admitting more gas from the cylinder. At higher pressures

the leak from the central electrode of the sparking plug necessitated a continuous small opening of the valve on the gas cylinder.

After the closing up of the reaction vessel the temperature was read at five minute intervals and when the pressure within began to rise this also was read at the same time. In this way pressure-time and pressure-temperature curves could be plotted from the readings. In order to eliminate one factor obscuring comparison - the rise of pressure due to heating of the gases and vapours - the pressures were reduced to zero Centigrade on the assumption that the simple gas laws were valid. This was only approximate but at the temperatures concerned 300 C to 500 C the laws can be applied with more accuracy than at lower temperatures. In this way a reduced pressure was obtained which corresponded fairly closely to the actual thermal effect on the shale. These are the pressures which are shown in the accompanying result sheets.

DETAILS OF EXPERIMENTS

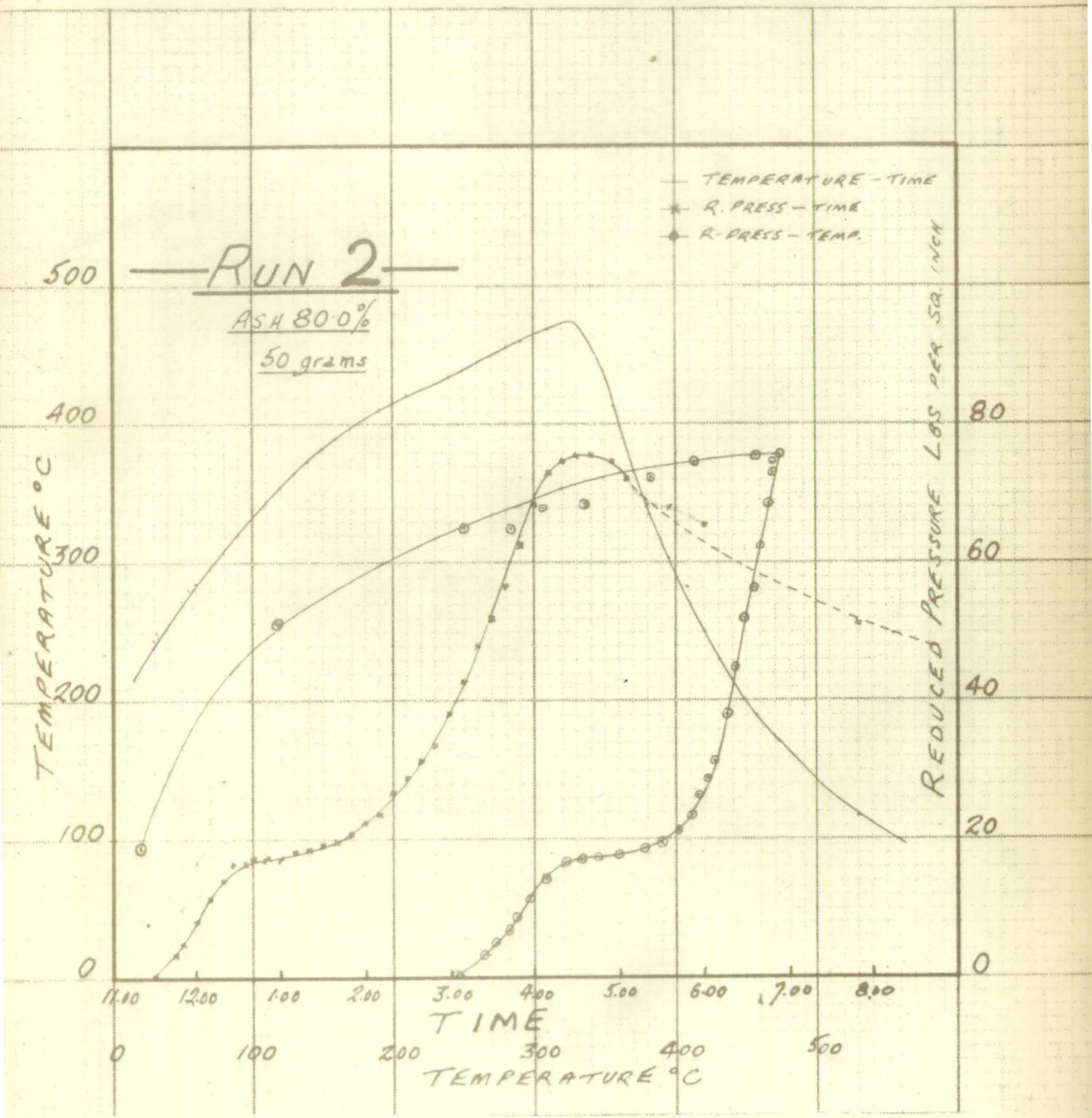
Eight different runs were made using two different samples of shale, one containing 80% ash and the other approximately 66% ash corresponding in laboratory distillation work to maximum yields of 24 and 53 gallons per ton respectively. The principal details of the runs can be seen from the following table

RUN No.	CHARGE	ASH IN SHALE	TEMP. OF CLOSING	REMARKS
1	20 gm.	80%	200 C	Gas gauge unsatisfactory
2	50 gm.	80%	200 C	Generally satisfactory
3	150 gm.	80%	200 C	Leak in gasket at 500 lb. press.
4	150 gm.	80%	200 C	Gas admission valve leaked
5	150 gm.	80%	200 C	Carbon dioxide cylinder too low in pressure to finish run.
6	100 gm.	81%	340 C	Satisfactory to 520 C. no cooling readings.
7	50 gm.	66%	327 C	Satisfactory
8	50 gm.	66%	200 C	Satisfactory in all respects.

RUN No. 2

Charge 50 grams of shale from Australian Shale Oil Corporation's lease, 80% ash, in ¼" flakes and dried to constant weight at 100 C Exhausted vessel to 40 m.m. pressure and closed off at 11.07 a.m. Cut off heating power at 4.30 p.m.

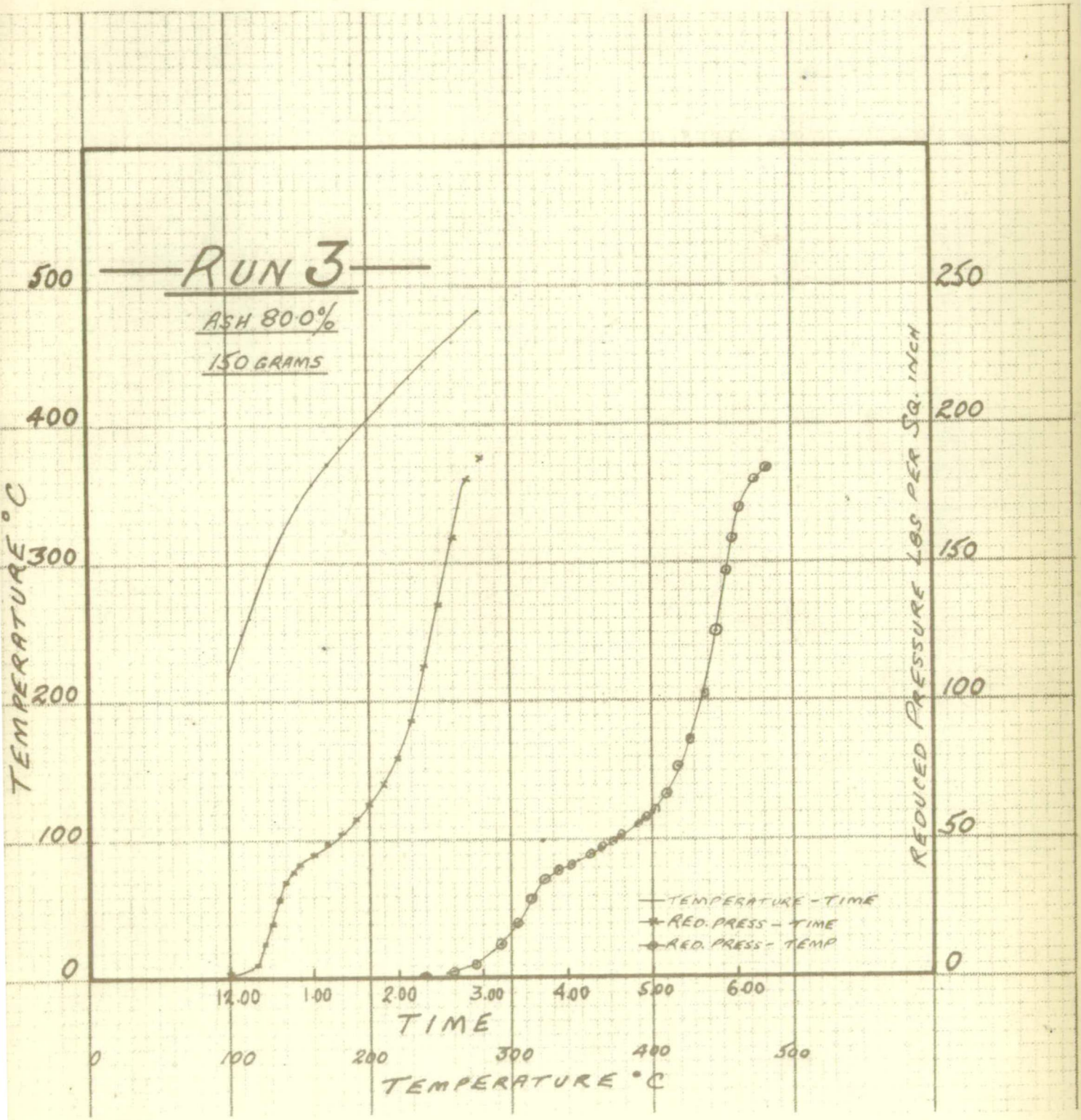
TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS/SQ. IN.	TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS/SQ. IN.
11.15	216	0.0	2.30	421	28.7
11.30	243	0.0	2.35	424	30.4
11.45	263	3.6	2.40	426	31.2
11.50	272	5.0	2.45	428	32.3
11.55	281	6.4	2.50	429	33.8
12.00	286	8.3	2.55	434	35.6
12.05	293	9.7	3.00	436	38.1
12.10	296	11.5	305	437	39.6
12.20	309	14.1	3.10	439	42.5
12.25	315	16.2	3.15	441	45.0
12.30	321	16.5	3.20	445	47.9
12.35	327	16.4	3.25	447	50.6
12.40	333	17.1	3.30	449	52.0
12.45	338	17.0	3.35	453	54.5
12.50	345	17.7	3.40	456	56.5
12.55	349	18.0	3.45	458	59.7
1.00	356	17.8	3.50	460	62.5
1.05	360	18.0	3.55	463	64.8
1.10	364	18.4	4.00	465	68.3
1.15	368	18.3	4.05	467	71.0
1.20	373	18.5	4.10	469	73.0
1.25	378	18.8	4.15	469	73.8
1.30	382	19.5	4.20	469	74.5
1.35	385	19.8	4.25	471	75.1
1.40	390	19.8	4.30	473	75.3
1.45	393	20.0	4.40	458	75.6
1.50	397	20.8	4.55	413	74.5
1.55	401	21.4	5.05	381	72.0
2.00	404	22.1	5.20	335	68.7
2.05	407	22.8	5.35	304	68.0
2.10	411	23.8	5.48	283	65.1
2.15	414	24.9	6.00	250	65.6
2.20	417	26.4	7.50	118	51.2
2.25	419	27.6	Next day	20	18.5


TEMPERATURE - TIME
R. PRESS - TIME
R-PRESS - TEMP.
RUN 2
ASH 80·0%
50 grams
TEMPERATURE °C
REDUCED PRESSURE LOSS PER SQ. INCH
TIME
TEMPERATURE °C
0
100
200
300
400
500
20
40
60
80
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00

RUN No. 3

Charge 150 grams of shale from Australasian Shale Oil Corpn's lease, 80% ash, in ¼" flakes and dried to constant weight at 100 C.
Exhausted to 40 m.m. and colsed off at 11.50 a.m.
Temperature at time of closing 200 C.
Run abandoned at 3.00 p.m. owing to leak developing.

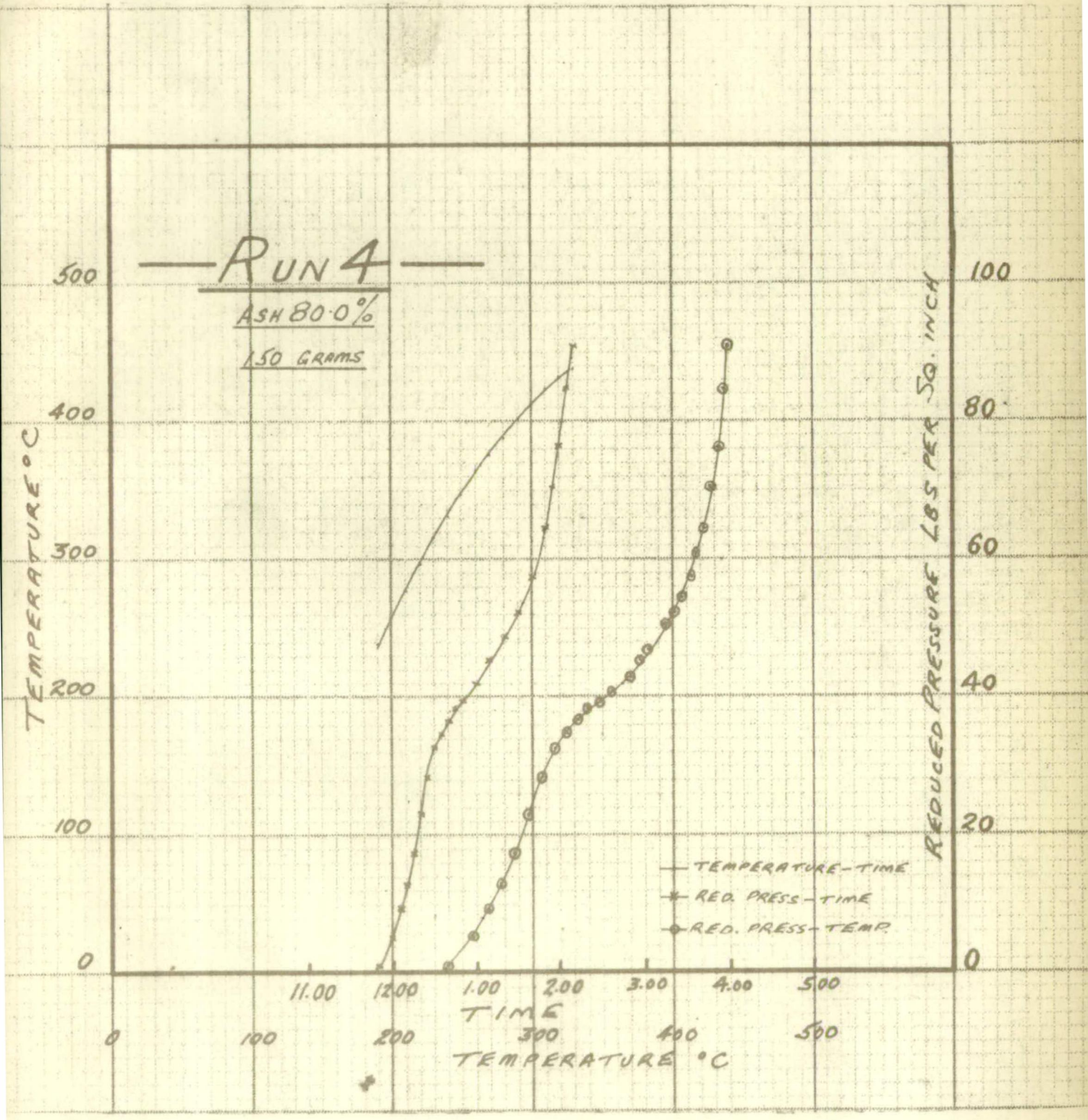
TIME	TEMPERATURE DEG. C	REDUCED PRESS. LBS./SQ. IN.
12.00	220	0.5
12.15	261	2.1
12.20	275	5.5
12.25	292	13.1
12.30	304	20.0
12.35	315	29.3
12.40	324	35.2
12.45	333	39.2
12.50	342	41.8
12.55	349	43.4
1.00	357	45.4
1.05	364	48.0
1.10	371	49.6
1.15	378	51.5
1.20	383	53.6
1.25	390	55.8
1.30	395	58.0
1.35	401	60.5
1.40	405	63.5
1.45	410	66.5
1.50	415	70.2
1.55	419	76.3
2.00	424	80.2
2.05	428	86.1
2.10	433	93.0
2.15	438	102.6
2.20	442	113.0
2.25	447	125.0
2.30	451	135.0
2.35	454	147.0
2.40	459	159.0
2.45	464	170.0
2.50	475	180.0
2.55	481	184.0
3.00	482	188.0


RUN 3
ASH 80.0%
150 GRAMS
TEMPERATURE °C
500
400
300
200
100
0
REDUCED PRESSURE LBS PER SQ. INCH
250
200
150
100
50
0
TEMPERATURE - TIME
RED. PRESS - TIME
RED. PRESS - TEMP
12.00
1.00
2.00
3.00
4.00
5.00
6.00
TIME
0
100
200
300
400
500
TEMPERATURE °C

RUN No. 4

Charge 150 grams of shale from Australasian Shale Oil Corporation's lease, 80% ash, in ¼" flakes, dried to constant weight at 100 C.
Exhausted to 80 m.m. pressure and closed off at 200 C.
Run abandoned at 2.10 p.m. owing to gasket blowing in admission valve.

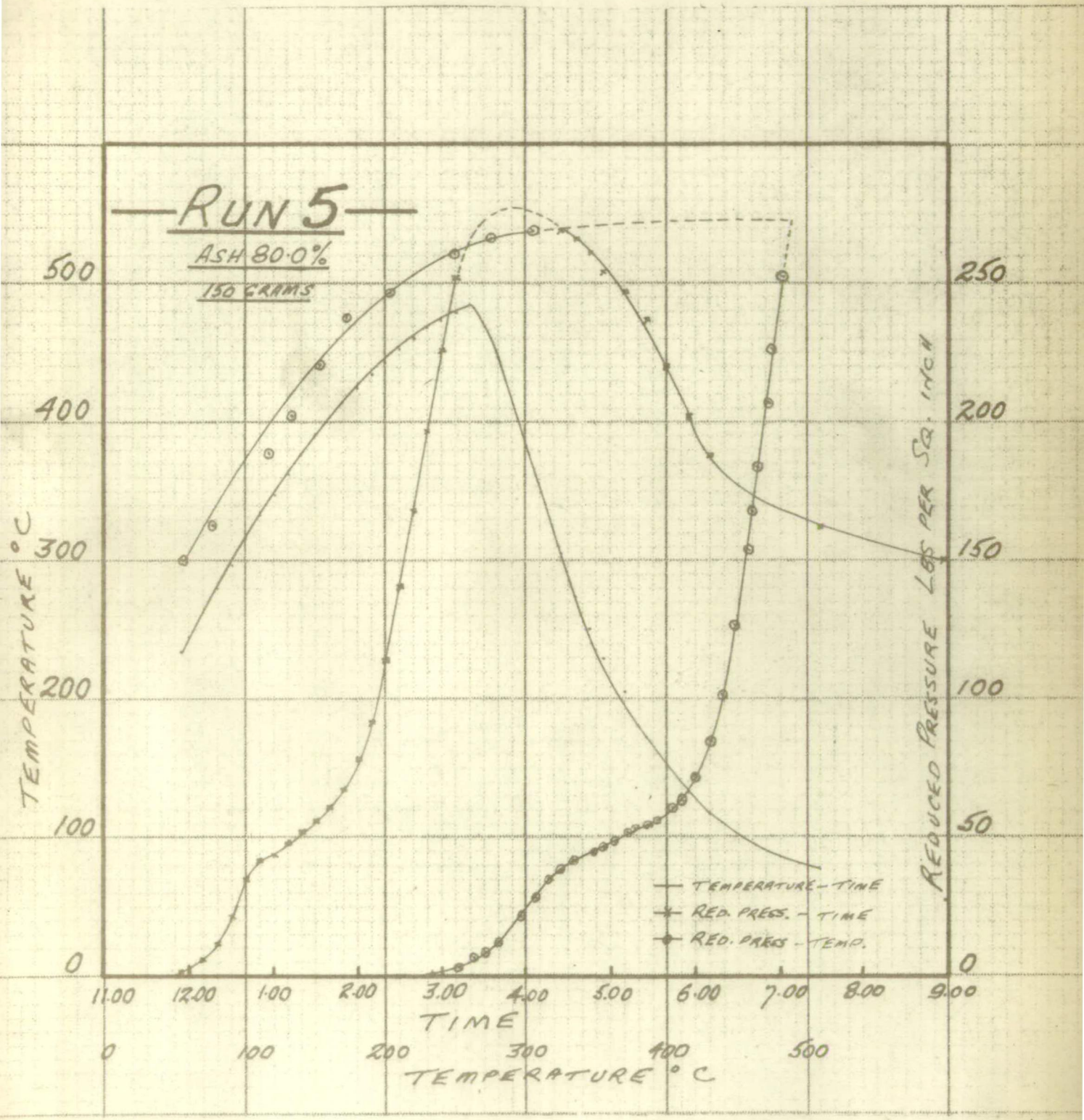
TIME	TEMPERATURE DEG. C	REDUCED PRESSURE LBS/SQ.IN.
11.50	239	0.9
11.55	248	3.7
12.00	258	5.7
12.05	269	9.6
12.10	278	12.9
12.15	287	17.5
12.20	297	23.0
12.25	306	28.3
12.30	317	32.4
12.35	325	34.8
12.40	331	36.5
12.45	339	38.5
12.50	347	39.6
12.55	356	40.8
1.00	363	42.0
1.05	370	43.3
1.10	376	45.8
1.15	382	46.8
1.20	389	48.8
1.25	395	50.6
1.30	401	52.1
1.35	407	54.5
1.40	413	57.7
1.45	418	61.0
1.50	423	64.5
1.55	427	70.5
2.00	431	76.2
2.05	436	84.8
2.10	439	90.8


RUN 4
ASH 80.0%
150 GRAMS
TEMPERATURE °C
500
400
300
200
100
0
REDUCED PRESSURE LBS PER SQ. INCH
100
80
60
40
20
0
TEMPERATURE-TIME
RED. PRESS-TIME
RED. PRESS-TEMP.
11.00
12.00
1.00
2.00
3.00
4.00
5.00
TIME
0
100
200
300
400
500
TEMPERATURE °C

RUN No. 5

Charge 150 grams of shale from Australian Shale Oil Corporation lease, 80% ash, in ¼" flakes, dried at 100 C.
Exhausted to 30 m.m. and closed off at 11.55 a.m. temperature 234 C.

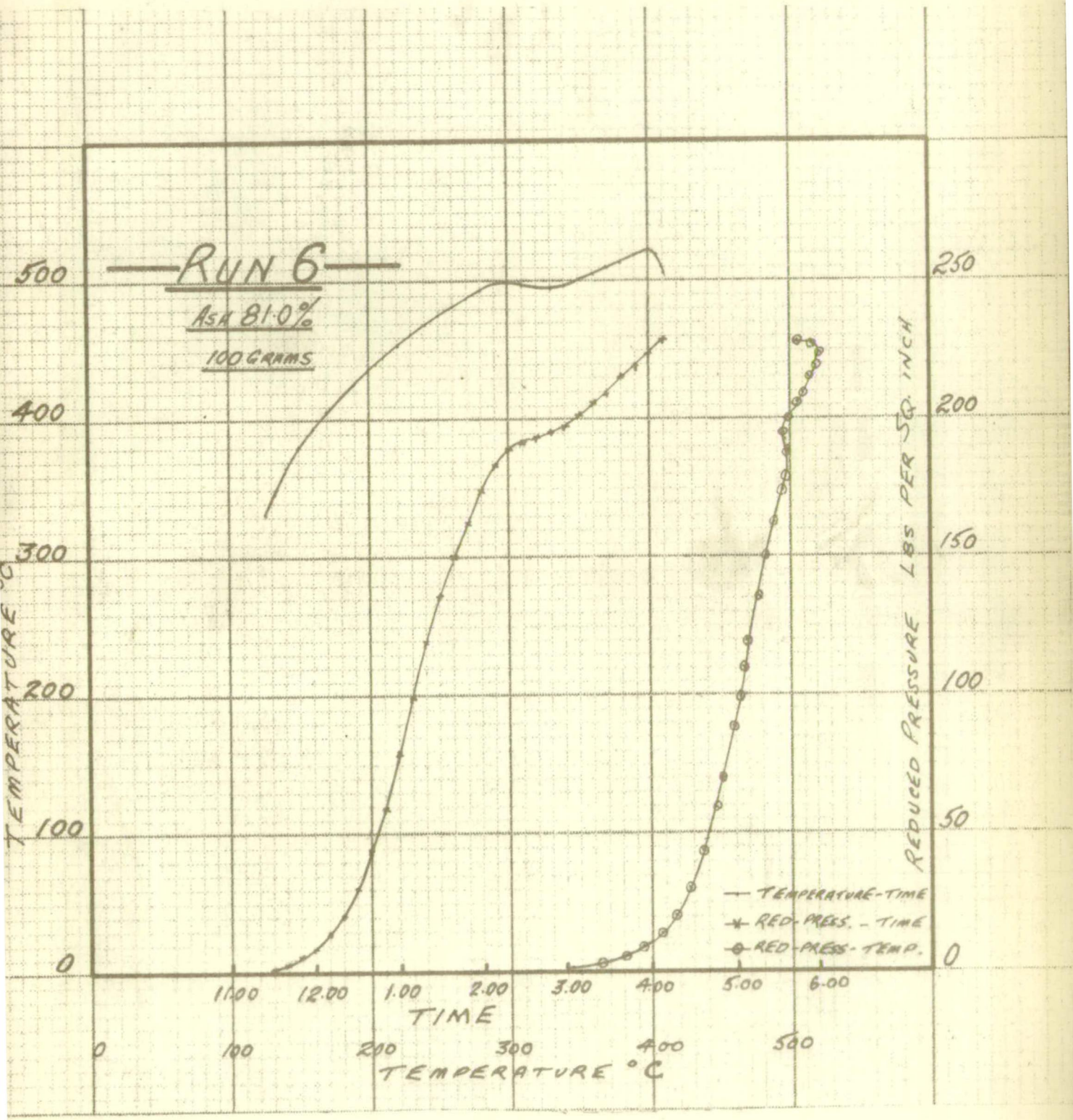
TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS./SQ.IN.	TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS./SQ.IN.
11.55	234	1.6	2.10	435	91.7
12.00	245	2.5	2.15	439	101.7
12.05	252	3.5	2.20	444	114.7
12.10	261	6.1	2.25	447	127.4
12.15	270	8.5	2.30	452	140
12.20	280	12.4	2.35	458	154
12.25	287	17.1	2.40	460	168
12.30	297	21.6	2.45	464	183
12.35	306	28.3	2.50	469	197
12.40	316	34.8	2.55	471	207
12.45	325	38.4	3.00	473	226
12.50	334	41.4	3.05	477	240
12.55	341	42.6	3.10	480	252
1.00	348	44.0	3.15	482	253½
1.05	355	46.0	3.20	485	press.not
1.10	363	48.4	3.40	447	measured
1.15	371	50.4	4.25	305	269
1.20	377	52.0	4.35	275	266
1.25	386	54.2	4.45	250	261
1.30	391	55.8	4.55	229	254
1.35	397	58.2	5.10	204	247
1.40	403	60.7	5.25	172	237
1.45	410	63.6	5.40	152	220
1.50	415	67.7	5.55	132	202
1.55	419	72.0	6.10	118	188
2.00	425	78.5	7.30	76	163
2.05	430	84.6	9.00	55	150


RUN 5
ASH 80.0%
150 GRAMS
TEMPERATURE °C
REDUCED PRESSURE LBS PER SQ. INCH
TIME
TEMPERATURE °C
TEMPERATURE - TIME
RED. PRESS. - TIME
RED. PRESS - TEMP.
500
400
300
200
100
0
250
200
150
100
50
0
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
0
100
200
300
400
500

RUN No. 6

Charge 100 grams shale from Australasian Shale Oil Corporation's lease, 80% ash, in ¼" flakes, dried at 100 C.
Needle valve closed at 11.15 after exhausting to 50 m.m. temperature 320 C.
Heating discontinued at 4.00 p.m.
Diaphragm gave out at 4.20 p.m.

TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS./SQ.IN.	TIME	TEMPERATURE DEGREES C	RED. PRESS LBS./SQ.IN
11.25	332	0.4	1.50	488	162.5
11.30	343	0.9	1.55	491	168.0
11.35	355	1.7	2.00	494	174.0
11.40	365	3.0	2.05	496	178.0
11.45	374	4.4	2.10	498	183.0
11.50	381	5.8	2.15	498	187.0
11.55	387	7.9	2.20	499	189.5
12.00	394	9.8	2.25	498	190.5
12.05	401	12.1	2.30	497	191.7
12.10	406	14.4	2.35	497	192.8
12.15	412	16.7	2.40	496	194.0
12.20	417	20.1	2.45	496	194.8
12.25	422	25.1	2.50	495	195.3
12.30	427	30.4	2.55	496	197.0
12.35	433	36.5	3.00	497	198.3
12.40	437	43.0	3.05	499	200.4
12.45	441	50.7	3.10	501	202.0
12.50	446	59.0	3.15	503	203.6
12.55	450	69.8	3.20	505	206.0
1.00	454	79.5	3.25	507	208.0
1.05	458	88.5	3.30	510	209.0
1.10	462	99.2	3.35	512	212.7
1.15	466	109.7	3.40	514	215.5
1.20	469	119.5	3.45	517	217.5
1.25	472	127.5	3.50	520	219.5
1.30	476	136.0	3.55	521	222.0
1.35	479	142.5	4.00	522	224.5
1.40	482	150.0	4.05	518	227.5
1.45	485	157.0	4.10	505	228.5

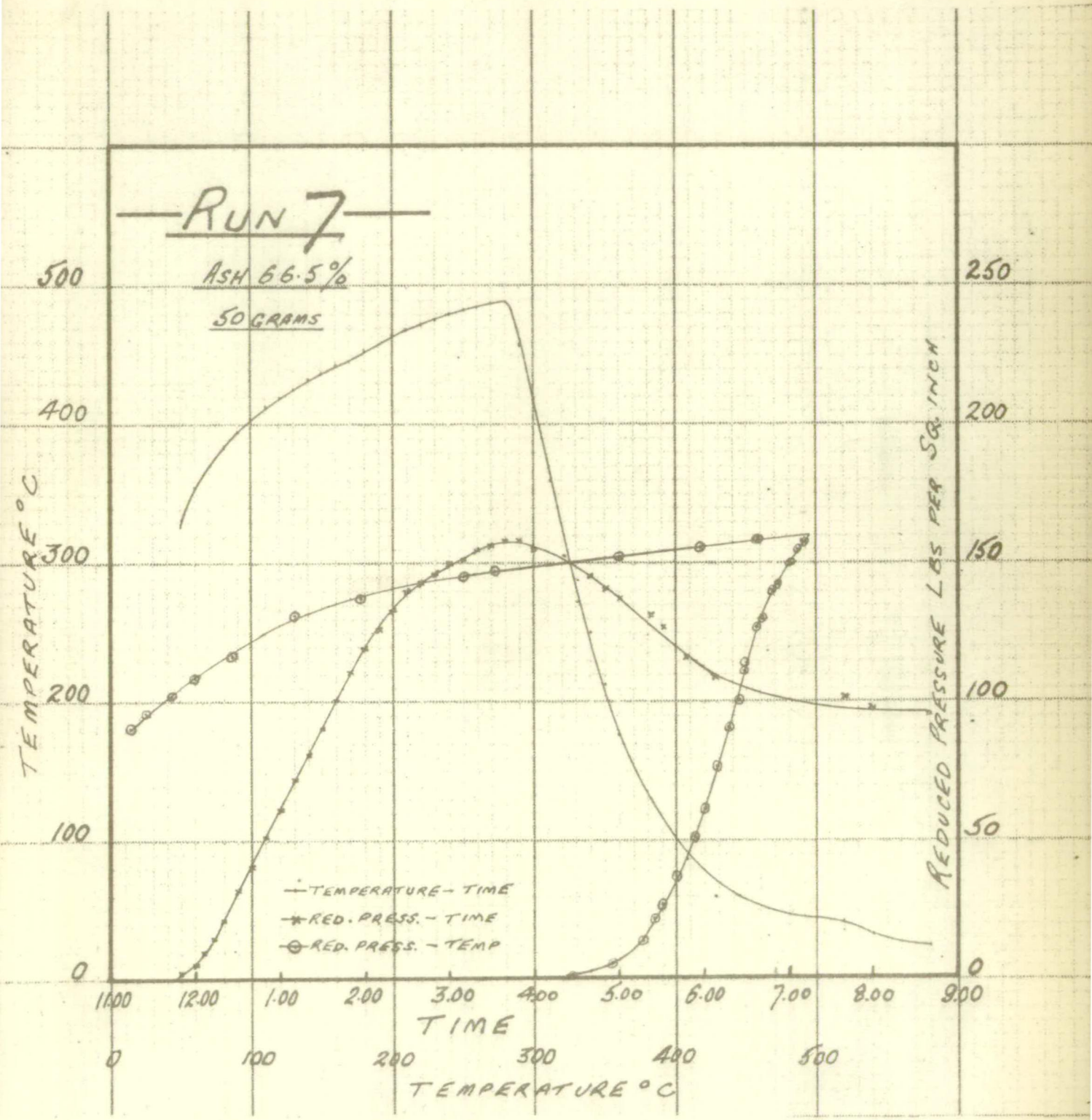

RUN 6
ASA 81·0%
100 GRAMS
500
400
300
200
100
0
TEMPERATURE °C
250
200
150
100
50
0
REDUCED PRESSURE LBS PER SQ. INCH
TEMPERATURE-TIME
RED-PRESS.-TIME
RED-PRESS-TEMP.
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
TIME
0
100
200
300
400
500
TEMPERATURE °C

RUN No. 7

Charge 50 grams of shale from the Tasmanite Shale Oil Co's mine ash 66.5%, in ¼" flakes and dried at 100 C.
Experienced trouble in closing needle valve which was not finally closed till 11.50 a.m. The temperature was 327 C and the shale was beginning to decompose appreciably. Pressure in vessel 90 m.m.

TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS./SQ.IN.	TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS./SQ.IN.
11.50	327	2.0	2.30	469	140.0
11.55	345	4.0	2.35	471	141.2
12.00	355	6.1	2.40	472	143.0
12.05	365	10.2	2.45	474	144.7
12.12	376	14.7	2.50	476	147.0?
12.17	382	19.5	2.55	478	148.1
12.20	384	21.6	3.00	480	149.8
12.25	390	26.8	3.05	481	151.2
12.30	395	32.6	3.10	482	152.0
12.35	400	36.6	3.15	483	154.2
12.40	404	40.3	3.20	485	155.0
12.45	408	46.0	3.25	487	155.2
12.50	413	50.9	3.30	489	156.5
12.55	416	55.3	3.35	491	157.2
1.00	420	61.3	3.40	489	158.3
1.05	423	65.8	3.50	458	158.5
1.10	426	72.1	4.00	418	155.5
1.15	429	77.0	4.11	360	152.0
1.20	433	81.5	4.22	305	149.3
1.25	436	87.3	4.31	272	147.5
1.30	438	90.5	4.40	250	145.0
1.35	441	95.5	4.50	212	140.3
1.40	444	100.8	5.00	176	137.0
1.45	446	105.3	5.10	152	135.0
1.50	448	111.0	5.22	130	131.3
1.55	450	113.8?	5.31	115	127.4
2.00	453	119.1	5.48	86	116.3
2.05	456	123.4	6.08	60	109.0
2.10	458	126.8	7.40	42	101.5
2.15	461	130.0	8.00	34	98.0
2.20	464	133.0	8.40	25	96.2
2.25	467	136.1	Next day	14	90.2

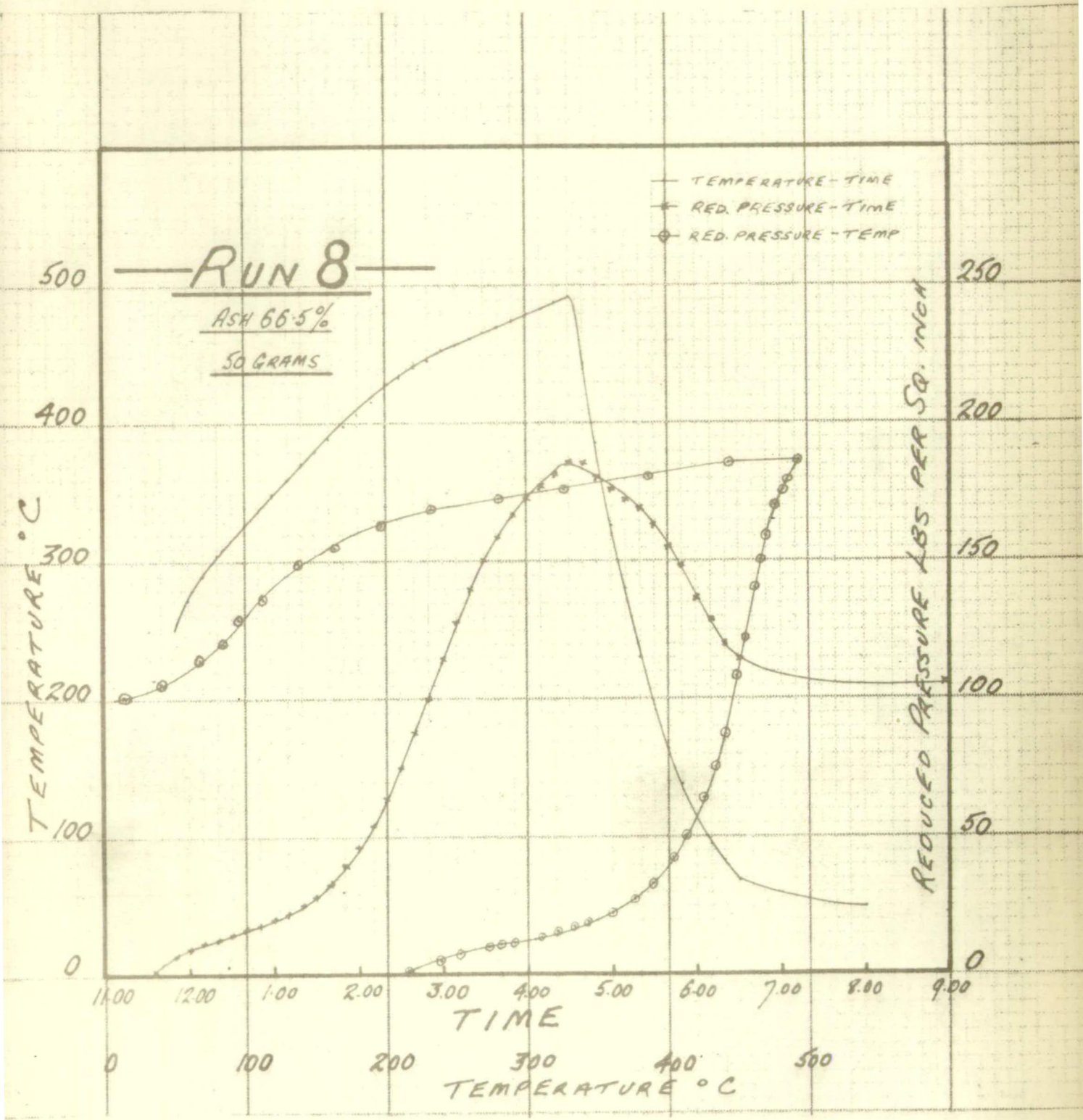
Heating power was switched off at 3.27 p.m. and accelerated cooling used by a gentle draught of air.
The two pressure readings are inaccurate owing to the thickness of the graduation stokes on the gauge.


RUN 7
ASH 66.5%
50 GRAMS
500
400
300
200
100
0
TEMPERATURE °C
250
200
150
100
50
0
REDUCED PRESSURE LBS PER SQ. INCH
TEMPERATURE - TIME
RED. PRESS. - TIME
RED. PRESS. - TEMP
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
TIME
0
100
200
300
400
500
TEMPERATURE °C

RUN No. 8

Charge 50 grams of shale from the Tasmanite Shale Oil Co's mine ash 66.5%, in ¼" flakes and dried at 100 C.
Exhausted to 80 m.m. and closed off at 11.30 a.m. the temperature being 200 C.
Heating power cut off at 4.25 and accelerated cooling used.

TIME	TEMPERATURE DEGREES C	RED. PRESS. LBS./SQ.IN.	TIME	TEMPERATURE DEGREES C	RED.PRESS. LBS/SQ.IN.
11.30	200	0.8	2.40	440	87.0
11.35	215	1.7	2.45	443	93.5
11.40	228	3.8	2.50	446	100.7
11.45	239	5.8	2.55	449	108.0
11.50	251	7.3	3.00	452	115.0
11.55	261	8.7	3.05	455	122.0
12.00	272	10.0	3.10	457	127.6
12.05	280	11.3	3.15	459	133.4
12.10	290	12.1	3.20	461	140.0
12.15	297	12.9	3.25	463	145.0
12.20	305	13.7	3.30	466	150.5
12.25	310	14.5	3.35	468	155.5
12.30	316	15.3	3.40	470	159.0
12.35	321	16.1	3.45	472	163.0
12.40	327	16.0	3.50	475	167.0
12.45	332	17.6	3.55	477	170.0
12.50	338	18.5	4.00	479	172.5
12.55	343	19.5	4.05	481	175.3
1.00	349	20.6	4.10	483	177.2
1.05	354	21.3	4.15	485	179.0
1.10	360	22.4	4.20	487	181.8
1.15	365	24.3	4.25	489	184.0
1.20	371	25.8	4.30	491	186.0
1.25	375	27.3	4.40	442	185.3
1.30	380	28.8	4.50	386	180.5
1.35	384	31.1	5.00	328	176.5
1.40	389	33.8	5.10	280	172.7
1.45	394	36.8	5.20	231	169.2
1.50	398	39.4	5.30	196	163.0
1.55	403	42.4	5.40	163	155.0
2.00	407	46.4	5.50	139.0	148.7
2.05	412	50.8	6.00	113	135.7
2.10	417	54.5	6.10	95	129.0
2.15	421	58.9	6.20	83	120.0
2.20	425	64.0	6.30	69	115.0
2.25	429	69.5	9.55	40	106.0
2.30	433	75.0	Next day	13	101.0
2.35	437	83.0			


TEMPERATURE - TIME
RED. PRESSURE - TIME
RED. PRESSURE - TEMP
RUN 8
ASH 66.5%
50 GRAMS
500
400
300
200
100
0
TEMPERATURE °C
250
200
150
100
50
0
REDUCED PRESSURE LBS PER SQ. INCH
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
TIME
0
100
200
300
400
500
TEMPERATURE °C

No.1 Run was only of the nature of a preliminary tryout though in general it was satisfactory except for a home made capillary pressure gauge proving troublesome. As the next run was very similar and was complete it alone has been reported.

Run No. 2 was generally satisfactory except that the millivoltmeter used for obtaining the temperature was not in the best of order and was not used again in following runs. The temperature could possibly have been carried a few degrees higher but otherwise no fault could be found.

Runs Nos. 3, 4, and 5 were rather abortive owing to troubles developing in the course of the run but the initial stages of decomposition of the shale were accurately obtained.

Run No. 6 was in general satisfactory except that no cooling readings were obtained.

Run No. 7 was the first run on a richer shale and was begun at 327 C when the initial stages of decomposition were over.

Run No. 8 was practically a duplicate of No. 7 for checking purposes except that the vessel was shut at 200 C to obtain the full decomposition curve.

Considerable disappointment was experienced with the pressure gauge used as it changed its zero in use considerably and no means were available in Tasmania for calibrating till after the work was finished. It was then found that the readings were inaccurate up to 20 atmospheres at which pressure the error was a maximum and amounted to 7% over the true pressure. The error then continuously diminished so that at 50 atmospheres the gauge again indicated the correct pressure. From 50 to 70 atmospheres the gauge indicated somewhat low being 1% in error at the latter pressure. These calibration results were obtained after the gauge had been used for a month at 60 to 80 atmospheres subsequent to this work. It would be a simple matter to correct the readings in accordance with an accurate calibration curve in my possession but I am sure that the gauge did not develop this inaccuracy in its first few times of use. For example before using it at all the gauge was checked at intervals up to 3 atmospheres against a mercury manometer and was found almost correct at all graduations. In all probability the gauge which was a specially made one, was correctly scaled at the time of manufacture but metal of unsuitable elastic properties had been used for the expansion tube.

No course seems open but to take the pressure figures as recorded at the time of the experiment with the consciousness that an error of several percent <u>may</u> exist in the readings from 5 to 40 atmospheres. The results thus lack quantitative accuracy to some extent but the main conclusions to be drawn are not affected

It became evident during the course of these runs that the shale oil produced was very easily decomposed and that maintaining the shale oil vapours and residue in contact in a closed vessel was completely changing the nature of the oil.

As regards throwing light on the nature of the oil or of the products to be obtained from shale in commercial extraction processes it was soon realised that this work was to a considerable extent ineffective. On this account the experiments were discontinued after the completion of the last of the eight runs as it was felt that further time expended would not be repaid in the results obtained.

DISCUSSION OF RESULTS

Preliminary work showed that once the ordinary moisture had been expelled by sufficiently long heating at 100 C, the shale suffered no further change resulting in loss of weight till a temperature approaching 250 C was attained. Most of the runs therefore were commenced at about 200 C.

Contrary to expectation the decomposition curve of the shale was in two distinct portions indicating that two distinct actions occurred. The first of these commenced with the poorer shale at 240 C and was complete at 320 C. Run 2 shows this initial decomposition most clearly as the average rate of heating in this temperature range was 1.3 degrees per minute whereas in Run 4 the heating rate in the corresponding range was 1.8 degrees. In run 2 the relatively small quantity of shale would lag only a few degrees behind the wall temperature of the vessel and thus the pressure-temperature curve is horizontal between 320 C and 340 C.

It can thus be inferred that the first decomposition is complete at approximately 320 C and that the rate of the second decomposition is comparatively small at 340 C but soon after becomes appreciable and between 360 C and 390 C averages 0.05 lbs per sq. in. reduced pressure per minute while from 440 C to 460 C the rate is 0.5 lbs per minute or approximately ten times as fast at 450 C as at 375 C.

The flattening of the pressure time curve indicated that the decomposition was complete or nearly so at 470 C, the slow rise in pressure of 0.05 lbs reduced pressure per minute at 470 C being partly due to cracking of the oil and partly due to further distillation of gas from the shale.

The temperature in this run was not carried above 473 C. The cooling curve showed no condensation at 458 C but at 413 C there was a reduction of 2.8% of the maximum reduced pressure. Condensation of the oil commenced therefore somewhat below 458 C but amounted to only several percent at 410 C. Thereafter by cooling to 20 C condensation equal to slightly over 75% of the maximum reduced pressure occurred.

The volume of the vessel was 336 m.l. and allowing for the volume of residue and oil which may be taken approximately as that of the original shale - 23 m.l. - gives 313 m.l. of gas at 1.26 atmospheres and 20 C which works out to 368 m.l. at N.T.P. The equivalent of this is 264 cu.ft. per ton at N.T.P. This gas yield is much lower than in ordinary atmospheric pressure distillation and may be partly accounted for by solution of low boiling hydrocarbons in the oil and absorption and adsorption on the residue.

With the larger charges of the same shale - 150 grams - the distinction between the first and second decompositions was not so clearly defined and this is undoubtedly due to the fact that the first decomposition had not been completed in the centre of the charge when the second decomposition commenced in the outer portion of shale. Working on information obtained from ordinary retorting and subsequent to these experiments it appears at this rate of heating - approximately 1.5 C per minute at 350 C in run No. 3 - a temperature gradient of nearly 27 C per inch existed with this size of shale viz. $\frac{1}{4}$" flakes. In the $\frac{3}{4}$" radius reaction vessel this corresponds to about 20 C and this would go far to run the two decompositions together so that Run 2 with a 50 gram charge is a more correct indication of the behaviour of the shale in this respect than Run 3.

In Run 3 the second decomposition thus follows very closely on the first while in Run 4 the first decomposition is not complete before the second commences. The rate of heating at 350 C in Run 4 was 1.6 C resulting in a larger temperature gradient which would have the effect of more markedly running the two decompositions togehter.

Run 5 shows also the running of the two decompositions together though not so markedly as Run 4. The heating rate for Run 5 at 350 C was 1.45 C per minute giving a behaviour similar to Run 3.

In Run 6 the first decomposition which had by this time been definitely linked with the expulsion of rather less than 0.75% of water from combination in the shale was cut out by closing the vessel offf at 340 C. This run showed no new features except that after the flattening of the pressure-time curve indicated the decomposition of the shale to be complete a gradual rise of reduced pressure which was increased by increased temperature clearly pointed to the cracking of the products of distillation.

Runs 7 and 8 were on a comparatively rich shale of approx. 66% ash. Run 7 was conducted without the first decomposition by closing off at 327 C. Except for a very small gasket leak as indicated by a slight smell the run was sufficiently close in behaviour to Run 8 to accept the latter as representing accurately the behaviour of this shale under this treatment.

As this shale was a rich one only 50 grams were used and with this quantity the maximum pressure recorded in Run 8 was 530 lbs. per square inch and was thus comfortably measured. In addition the apparatus had benefited by the previous experience and the run was quite trouble free.

The plotted results show the first decomposition less plainly than in the case of the poorer shale under nearly similar conditions - Run 2 ~~8~~ viz. 50 gram charge and heating rate in the 240 to 320 C range, 1.3 C and this may partly be accounted for by the fact that in the same temperature range the heating rate was 1.6 C in Run 8.giving a greater temperature gradient. Later work on this shale showed that the first decomposition is not completed in eleven hours at 300 C but is nearly so at the end of 44 hours while one hour at 350 C is nearly as effective as the 44 at the lower temperature. The first decomposition would therefore only be complete when the shale had reached 350 C or even 360 C and at these temperatures the general pyrolysis of the kerogen would have commenced. However the first action is discernable and is of the same order as in the case of the poorer shale - approximately 16 lbs. reduced pressure for 50 grams of shale which may be explained by the expulsion of a similar amount of water from the shale in this range.

The second decomposition becomes appreciable in the vicinity of 350 C and is shown by the curve to be of the usual form. The total reduced pressure reached 186 pounds per square inch or 5.5 lbs. per 1% kerogen in this rich shale as against 76 lbs. or 3.8 lbs per 1% kerogen in the case of the poorer shale. The poorer shale was later found to be of an unusual type for this field giving an oil low in sulphur and containing a much smaller proportion of unsaturated hydrocarbons.

In Run No. 8 the uncondensed gas was 310 m.l. at 13.5 C and 6.87 atmospheres equivalent to 2030 m.l. at N.T.P. or 1460 cu.ft. under standard conditions.This amount of gas does not greatly exceed that produced under atmospheric pressure distillation at the same rate of heating. It must however be borne in mind that at this pressure the lower boiling hydrocarbons would be in solution in the oil or absorbed by the residue so that the amount of gas under equilibrium conditions at atmospheric pressure would be considerably larger.

The nature of the oils produced in these pressure retortimgs was not very fully investigated but in general were very similar to a vapour phase cracked oil such as that produced in Run 33 on which more work was done.

A comparison of the distribution of the kerogen into the various divisions in both constant volume and constant pressure retorting is of interest and is shown in the following table.

WEIGHT DISTRIBUTION OF PRODUCTS OF RETORTING

Comparison expressed as percentages of original shale

	Run 8	Run 33	Run 15
Volatiles in residue	4.58	4.35	3.36
Fixed carbon in residue	5.76	5.95	3.10
Oil	12.0	13.60	21.72
Gases water etc	11.56	9.60	5.30
Ash	66.1	66.5	66.52
	100.0	100.0	100.0

Comparison expressed on an ashless basis (kerogen).

	Run 8	Run 33	Run 15
Volatiles in residue	13.5	13.0	10.0
Fixed carbon in residue	17.0	17.75	9.25
Oil	35.4	40.6	64.9
Gases water etc.	34.1	28.65	15.85
	100.0	100.0	100.0

Run 15 represents distillation of this standard sample of shale under optimum conditions as found in the later work reported in Part III. In Run 33 the oil vapours were vapour phase cracked at 560 C with 5 to 8 seconds contact of vapours and cracking residue. It will be seen by reference to the above tables that constant volume retorting of the shale even when the temperature is only carried to a very moderate limit - 491 C - is very destructive as regards the oil both in quantity and in character as compared with distillation under atmospheric pressure.

The comparative distillation analyses of the oils produced in the same three runs are of interest and are as follows

	Run 8	Run 33	Run 15
Below 150 C	21.6%	23.6%	11.1%
150 C to 200 C	10.8	14.0	10.7
200 C to 250 C	10.8	10.7	9.6
250 C to 300 C	12.2	18.5	12.7
Residuum	44.6	33.3	55.9
	100.0	100.0	100.0

After the completion of Run 8 further work on these lines was discontinued as it was considered that most of the useful information obtainable had already been obtained from these experiments and attention was directed to other channels of investigation. The later work reported in Part III on vapour phase cracking yielded an interesting comparison with this work as shown in the tables above. Vapour phase cracking for a short time at a higher temperature will yield more oil and of a better quality than constant volume retorting and at the same time dispense with the difficulties inherent in work at higher pressures than atmospheric. In both cases the oil becomes enriched in sulphur owing to the greater thermal stability of the heterocyclic sulphur compounds produced by the pyrolysis of the kerogen as compared with the non-sulphurous hydrocarbons which make up the bulk of the oil. As might be expected the oils produced in both constant volume retorting and by vapour phase cracking are much higher in aromatic content than normal shale oil.

PART II

FURTHER STUDY OF THE PYROLYSIS OF THE OIL PRODUCING MATERIAL IN TASMANITE

The production of oil and soluble bitumen by the pyrolysis of certain Continental, American, and New South Wales oil shales is the subject of an article by R. H. McKee and E. E. Lyder in the Journal of Industrial and Engineering Chemistry Vol. 13, 1921, pages 613 and 678. This article was not discovered till the work described hereunder was practically complete. There is a general similarity between the above quoted work and that to be described but the methods of investigation are rather different. This work was undertaken to throw some light on the behaviour of Tasmanite in retorting and naturally is of direct local interest.

EXPERIMENTAL

The general procedure was to place 10 grams of shale - the standard sample referred to in Part III - of approximately 66% ash, crushed through 20 mesh and dried to constant weight by some hours heating at 100 C, in a hard glass test tube and then to draw out the tube leaving an exit for gas and oil approximately 3 m.m. diameter. The retention of the volatile products in the tube was considered and abandoned because of the action these products have on the kerogen in promoting greater solubility when maintained in contact at temperatures of 350 C and over. It was considered that more parallel behaviour to actual retorting would be obtained by allowing them to escape.

The tube containing the weighed shale was then inserted in a steel tube placed in a tubular electric furnace 20 inches long which had a constant temperature zone at least twice the length of the shale tube itself which was placed in the centre of the zone. The metal tube was used to secure uniformity of temperature with greater confidence. An iron-constantan thermocouple in contact with the glass tube gave the temperature of the latter.

The temperatures selected were 300 C and 350 C as action on the shale is relatively slow at these temperatures. At 300 C the shale was comparatively unaffected losing 4.25% of its weight in 44 hours. Heating of another sample for no less than 220 hours only increased the loss to 4.60% so that it appears

that at 300 C the first decomposition noted in Part I is completed if sufficient time be allowed at this temperature while the rate of the second decomposition (that of the kerogen) is very small.

At 350 C action on the shale is moderately slow but not by any means inconsiderable. The main bulk of this work was therefore confined to 350 C. At 400 C action is rapid relatively to that at 350 C. One heating at 400 C was carried out to gain some idea of the relative velocity of decomposition at 350 C and 400 C.

The general procedure was to heat the shale for the given time at the appropriate temperature and after cooling weigh the residue to determine the loss on heating. The residue was then extracted with carbon disulphide dried and weighed. Proximate analysis of the dried residue was then made to enable the fixed carbon, volatile matter, and the ash to be calculated to the original shale. Working in this way a check on the uniformity of the shale sample was obtained.

Although the original shale sample was large enough for the whole of this work and was crushed through 20 mesh, a large proportion being much finer, and the sample thoroughly mixed, the ash varied in the extreme cases from 64.6% to 66.7% with most of the samples falling between 65.8% and 66.2%. There is a little uncertainty attached to the meaning of ash in the case of this shale as the ash depends on the conditions under which the volatile matter is expelled. Under oxidising conditions a higher ash results so all ashes were determined in the course of the proximate analyses which gives consistent results. Another source of error is the rapidity with which the shale powder picks up about 1% of moisture. The variations in ash found are partly attributable to the fact that the shale sample was representative of a large quantity and certain richer laminae or parts were tough and flaky and the other poorer material much softer so that a little greater preponderance of rich flaky material would lower the ash which seems to have occurred in one or two cases. In addition it was impossible to remove all the extracted shale from the extraction thimble introducing a little uncertainty as the finer material which penetrates into the thimble wall is higher in ash and the nett effect is to show a lower ash than really the case.

I hardly believe the ash variations on different portions of a thoroughly mixed sample could be as great but I have accepted them as real and in the second portion of the tabulated results calculated all quantities to an ashless basis for comparison.

The average ash works out to 66.05% as against 66.5% on the raw dry shale which bears out the enrichment idea to an extent. The variations are not sufficient to affect the main conclusions drawn especially in regard to the loss on heating and extraction.

The following is a summary of the various heatings and extractions carried out together with brief explanatory notes.

HEATING TEMPERATURE 300 C.

No. 1. Charge 10 grams. Heating time 44 hours. Temperature maintained within 2 degrees of 300 C for whole time.

No. 2. Charge 10 grams. Heating time 220 hours. Temperature maintained within limits 297 C - 300 C for whole time. The shale darkened somewhat and a slight carbonaceous film was left on the glass.

HEATING TEMPERATURE 350 C.

No. 3. Charge 10 grams. Heating time 1 hour after allowing 15 minutes in the hot tube to reach 350 C.

No. 4. Charge 10 grams. Heating time 5 hours. Temperature rose to 360 C for a few minutes but otherwise would average close to 350 C. Shale browned but not very much changed in appearance.

No. 5. Charge 10 grams. Heating time 10 hours. Temperature rose to 360 C for a short time and for most of the time was at 345 C. The nett effect would be close to 10 hours at 350 C.

No. 6. Charge 10 grams. Actual time of heating 16½ hours but the temperature was down to 335 C for part of the night. The nett effect was probably only equivalent to 12 hours at 350 C.

No. 7. Charge 10 grams. Heating time 20 hours. The temperature would perhaps average closer to 348 C than 350 C but was comparatively constant and for this reason was not altered. This run gave a lower loss on heating as a smaller than usual exit hole hindered the escape of oil vapours.

No. 8. Charge 10 grams. Heating time 20 hours. Temperature did not exceed 350 C and would average 349 C.

No. 9. Charge 10 grams. Heating time 20 hours. Temperature up to 360 C for a short time but total effect not very different from 20 hours at 350 C.

Note These details for experiments 8 and 9 should be interchanged owing to a typographical error.

No. 10. Charge 10 grams. Heating time 30 hours. Temperature closely controlled.

No. 11. Charge 10 grams. Heating time 30 hours. Temperature closely controlled. The gas exit was too small resulting in a lower loss on heating - compare No. 7.

No. 12. Charge 10 grams. Actual heating time 40 hours. The temperature was variable and up to 363 C - 366 C for 6 hours. The total effect may have easily been equal to more than 50 hours at 350 C.

No. 13. Charge 10 grams. Heating time 50 hours. Temperature somewhat variable 343C to 357 C but nett effect would not be much different from 50 hours at 350 C. The residue was black like an ordinary distillation residue and the glass was coated with a coherent film of carbon.

HEATINGS AT 400 C.

No. 14. Charge 10 grams. Heating time 2 hours. Shale blackened and ina bituminous cake flowing slowly while hot like asphalt concrete.

As a check on the nett effect of the heat 10 grams of raw shale dried at 100 C were extracted with carbon disulphide.

Larger scale distillations at 300 C.

Two larger scale distillations in which the products expelled were condensed were carried out. These were

Run A This was abandoned after 10 hours heating as the temperature ran up to 350 C for an houb or so. Certain data were obtained and are given below

Charge 200 grams dried shale		
Water produced	2.6 grams	1.3 %
Oil produced 1.1 m.l.	1.0	0.5
Residue weight	194.5	97.25
Gas by difference	1.9	0.95
	200.0	100.0

RUN B

In this run the temperature averaged slightly below 300 C for about 10 hours running up to 310 during one hour. The actual effect of heating would be very nearly equivalent to 11 hours at 300 C. No water was produced after the first hours heating and the trace of oil was likewise expelled in the first 2 hours.

The weight balance is as follows

Residue	196.1 grams	98.05%
Water	2.0	1.0
Oil	0.3	0.15
Gas	1.6	0.80
	200.0	100.0

No hydrogen sulphide was produced in either of these distillations at 300 C as the sodium hydroxide liquor through which the gas was passed showed no increase in its small sulphur content.

Proximate Analyses of extracted residues

The following are the proximate analyses of the residues from the various experiments after extraction with carbon disulphide.

No. of Expt.	Temperature	Time of heating	Total loss heat.& ext.	Res. %	Vol.	Fixed Carb.	Ash
Raw	-	-	1.0	99.0	31.0	1.75	67.25
A	300	11 hrs	2.67	97.33	28.2	2.7	69.1
1	300	44	4.75	95.25	26.05	4.5	69.45
2	300	220	4.9	95.1	23.7	6.7	69.6
3	350	1	4.9	95.1	27.5	2.5	70.0
4	350	5	9.0	91.0	20.35	5.4	74.25
5	350	10	16.4	83.6	18.05	2.85	79.1
6	350	12?	19.7	80.3	14.8	3.4	81.8
7	350	20	30.35	69.65	6.45	0.9	92.65
8	350	20	27.6	72.4	6.5	2.7	90.8
9	350	20	27.05	72.95	6.7	2.45	90.85
10	350	30	26.3	73.7	7.2	4.4	88.4
11	350	30	25.2	74.8	8.55	2.3	89.15
12	350	40	21.2	78.8	7.8	8.65	83.55
13	350	50	20.0	80.0	8.5	8.4	83.1
14	400	2	29.3	70.7	5.6	0.8	93.6

TABULATED GENERAL RESULTS

Expressed as a percentage of original shale

No.of Expt.	Temperature	Heat. time	Heat. loss	Extn. loss	Total loss	Vol.in Res.	Fix. C in Res.	Ash in Residue
Raw	-	-	-	1.0	1.0	30.75	1.75	66.5
A	300	11	2.0	0.7	2.7	27.45	2.65	67.2
1	300	44	4.25	0.5	4.75	24.8	4.3	66.15
2	300	220	4.6	0.3	4.9	22.55	6.35	66.2
3	350	1	3.8	1.1	4.9	26.1	2.4	66.5
4	350	5	6.4	2.6	9.0	20.8	4.75	65.45
5	350	10	8.8	7.6	16.4	15.1	2.4	66.1
6	350	12?	9.6	10.1	19.7	11.9	2.7	65.7
7	350	20	12.65	17.7	30.35	4.5	0.6	64.55
8	350	20	17.45	10.15	27.6	4.7	1.95	65.75
9	350	20	17.75	9.3	27.05	4.8	1.80	66.3
10	350	30	17.0	9.3	26.3	5.3	3.25	65.15
11	350	30	11.4	13.8	25.2	6.4	1.7	66.7
12	350	40	20.2	1.0	21.2	6.15	6.8	65.85
13	350	50	17.2	2.8	20.0	6.8	6.7	66.5
14	400	2	15.3	14.0	29.3	3.9	0.6	66.2

TABULATED GENERAL RESULTS

Expressed as a percentage of the kerogen - ashless basis

No.of Expt.	Temperature	Heat. time	Heat. loss	Extn. loss	Total loss	Vol.in Res.	Fix. C in Res.	Ash in Residue
Raw	-	-	-	3.0	3.0	91.75	5.25	
A	300	11	6.1	2.15	8.25	83.55	8.10	
1	300	44	12.55	1.50	14.05	73.25	12.7	
2	300	220	13.6	0.9	14.5	66.7	18.8	
3	350	1	11.4	3.3	14.7	78.1	7.2	
4	350	5	18.6	7.45	26.05	60.2	13.75	
5	350	10	26.0	22.4	48.4	44.55	7.05	
6	350	12	27.95	29.4	57.35	34.75	7.9	
7	350	20	35.65	49.95	85.6	12.7	1.7	
8	350	20	51.0	29.6	80.6	13.7	5.7	
9	350	20	52.75	27.65	80.4	14.25	5.35	
10	350	30	48.8	26.6	75.4	15.25	9.35	
11	350	30	34.2	41.5	75.7	19.2	5.1	
12	350	40	59.3	2.8	62.1	18.0	19.9	
13	350	50	52.2	7.45	59.65	20.3	20.05	
14	400	2	45.3	41.4	86.7	11.5	1.8	

Discussion of Results

HEATINGS AT 300 C

The results in general exemplify the usual enormous increase in the velocity of chemical change with temperature. In the constant volume work it was seen that there were two distinct actions taking place - the lower temperature one beginning in the region of 240 C and being completed by about 320 C. This action was closely followed by another one as most clearly shown in Run 2 - Part I of this work. In Run 8 the shale used was from the same lot as that used for these extraction experiments and the two decompositions blend into one another, the junction being barely perceptible.

The experiments at 300 C deal with the first of these actions and it will be seen that at 300 C a considerable time is required for its completion.

The raw dry shale yields a peculiarly smelling extract of viscous oily material interspersed with crystals and not at all like shale or mineral oil. At the time of writing the nature of this material has not been investigated but it is thought that it is an unchanged plant product that has survived the geological ages. Its weight is very closely 1% of the shale or 3% of the kerogen. This material is slowly volatilised, at least, in part and is the source of the very small quantity of oil produced at 300 C. The quantity of extractable matter therefore decreases with the time of heating at 300 C.

The shale gradually loses weight on heating, and in 11 hours at 300 C 1% of water is given up, 0.15% of oil, and 0.80% by weight of gas largely consisting of carbon dioxide but containing no hydrogen sulphide. On further heating at this temperature the shale suffers slow change and gives off carbon dioxide with possibly a little water vapour.

Heating for 44 hours at 300 C practically completes the primary decomposition as comparatively little further change occors even on prolonging the heating to 220 hours.

The fact that no hydrogen sulphide is produced at 300 C indicates that the real pyrolysis of the spore material has not commenced at this temperature but a distinctly independent change has occurred involving the expulsion of water and carbon dioxide.

Judging on the combined loss on heating plus extraction one hour at 350 C is somewhat more effective than 220 hours at 300 C in completing the primary decomposition.

Slow heating of the shale or heating at 300 C for long periods also brings about internal change in the kerogen material so that on subsequent distillation much more carbonaceous material is left in the residue. The conditions in a platinum

crucible during a proximate analysis are certainly not parallel with commercial or laboratory distillation but certain facts are worthy of notice.

The fixed carbon left at 900 C expressed as a percentage of the kerogen in this particular sample of shale - the standard one used in many of the distillations in Part III - and calculated from the proximate analysis of the residue and its percentage of the shale rarely falls below 10 % for laboratory distillation under optimum conditions and is larger than this under slower distillation whether laboratory or commercial yet by simple ignition of one gram in a covered crucible only 5% of the kerogen appears as fixed carbon with ignition temperature of 900 C. This has been verified many times and has been the incentive to study the shale under high rates of heating in distillation as in Part III.

Now at 300 C there is comparatively little of an oily character expelled from the shale but a definite internal change in the kerogen material takes place which results in the production of more fixed carbon on ignition of the residue after extraction. Heating for 11, 44, and 220 hours respectively at 300 C increases the fixed carbon from 5.25% to 8.1%, 12.7%, and 18.8% respectively.

It seems quite well established that heating for long periods even at 300 C is detrimental to the oil yield on subsequent distillation. This confirms the observations that in ordinary retorting, slow distillation - the shale passing through the distillation range in 5 hours - produces about 10% less oil than a one hour distillation on the same sample.

Acceleration of the gas flow by steam to reduce the vapour phase cracking in the retort to several percent of that obtaining in simple distillation and therefore practically to a negligible quantity , fails to bring up the oil yield to that of a fast simple distillation although recovering about half of the 10% difference. The remaining discrepancy is apparently due to the change in the kerogen material resulting in the greater production of fixed carbon and possibly gas but not oil.

HEATINGS AT 350 C.

The total loss on heating plus extraction is about the same for experiments 2 and 3 suggesting that action on the shale is about 200 times or 250 times as fast at 350 C as at 300 C. This really applies to the first decomposition.

At 400 C the velocity of change is approximately 10 times as fast as at 350 C as may be seen by comparing experiments 7, 8, and 9 with 14. This ratio applies to the second decomposition or the real pyrolysis of the kerogen.

At 350 C it was sufficiently slow to lend itself to observation and yet fast enough for convenient study.

The total thermal effect on the shale appears to be best

measured by the loss on heating plus that on extraction since the relative proportions of these two is governed by the conditions of exposure. Approximately constant conditions of exposure are needed as the prevention of escape of the oil vapours promotes solubility of the remaining kerogen material as for example experiments 7 particularly and to a lesser degree 11.

The general results are shown in the accompanying graph where the total loss on heating plus extraction is plotted against time of heating. From one to twenty hours heating the effect is closely a straight line function of the heating time and instead of the thermal effect decreasing as the kerogen material becomes exhausted the rate is maintained approximately constant. This appears to be due to the oils produced on pyrolysis promoting solubility of the remaining kerogen material and fully compensating for the exhaustion of the parent substance. In drawing the curves from relatively few points it is difficult to draw one free from criticism and so the ones drawn indicate rather the general trend than anything absolute. Experiment 12 is hardly worth considering in drawing the curves as the temperature was too high for a period giving a total effect more like experiment 13.

After 20 hours at 350 C the kerogen material is largely changed into gases and bituminous oils so that further heating only results in the distillation off of oil and gas and the production of fixed carbon. This is clearly shown by the downward trend of the curve in question.

As regards the fixed carbon calculated from the residue weight and proximate analysis the curve shows a contrary flexure. Were no oil removed by extraction of the residue from heating the form of the curve would no doubt be similar to that shown for the ∠ 300 C heatings only with the magnitudes greater for the higher temperature. This curve is shown in broken line. The departure from this simpler form is due to the removal by extraction of bituminous substance which would naturally produce a good proportion of fixed carbon on slow distillation. This removal by extraction was of a not an important factor in the 300 C experiments on account of the small amount of extractable material present.

In this way the potential fixed carbon left in the residue passed through a minimum value for the 20 hours time of heating since this time is the most effective in making the kerogen soluble but with the longer heating periods the value largely increases. The effect of heating in making potential fixed carbon is clearly seen in the initial downward trend of the

fixed carbon curve where one and five hours heating increase the fixed carbon in the residue expressed as a percentage of the kerogen from 5.25% to 7.2% and 13.75% respectively. This is precisely the same effect as discussed before only the action is much more rapid at 350 C than at 300 C. It so definitely occurs with 5 hours heating in which time about three quarters of the kerogen is yet unaffected that the preliminary warming up period of the shale in a commercial retort undoubtedly adversely affects the oil yield to the extent of nearly 5% of the maximum possible oil yield in rapid distillation.

HEATING TEMPERATURE 400 C.

Action was too rapid at this temperature to carry out with much accuracy a series of heatings in the apparatus used for the foregoing work. However one experiment at 400 C with 2 hours heating time showed that 86.7% of the kerogen material was affected which is somewhat greater than the maximum found at 350 C. On the whole the result was very similar to that of experiment 7 where the exit was partially blocked. After extraction the fraction of the original kerogen material remaining was 13.3% the corresponding figure for experiment 7 being 14.4%. These figures may be compared with the 19% - 26% remaining after distillation at atmospheric pressure under various conditions. It is thus seen that by certain heat treatment followed by extraction of the bitumen produced a greater proportion of the kerogen can be removed than by direct distillation even under reduced pressure.

NATURE OF BITUMEN EXTRACTED

Extraction of the shale residues was carried out in an electrically heated Soxhlet apparatus. The evaporated extracts gave a dark brown substance to the eye and simple tests identical with ordinary bitumen remaining from the distillation of asphaltic base mineral oils. This bitumen does not exist in the shale as such but is produced by the pyrolysis of organic matter of which the most important variety is the spore case material which appears to be akin to amber. The spore case material in this sample of shale contains no less than 4.6% of sulphur so that it is not surprising that the bitumen should be rich in sulphur. The sulphur content of a composite sample of the extracted bitumen was 5.6% so that the sulphur content of the ordinary shale oil produced by the cracking of the bitumen which is about 2.2% when free from hydrogen sulphide

appears relatively moderate. The great reduction in the sulphur content of the oil compared with the bitumen is due to the disengagement of a relatively large amount of hydrogen sulphide in the cracking of the bitumen.

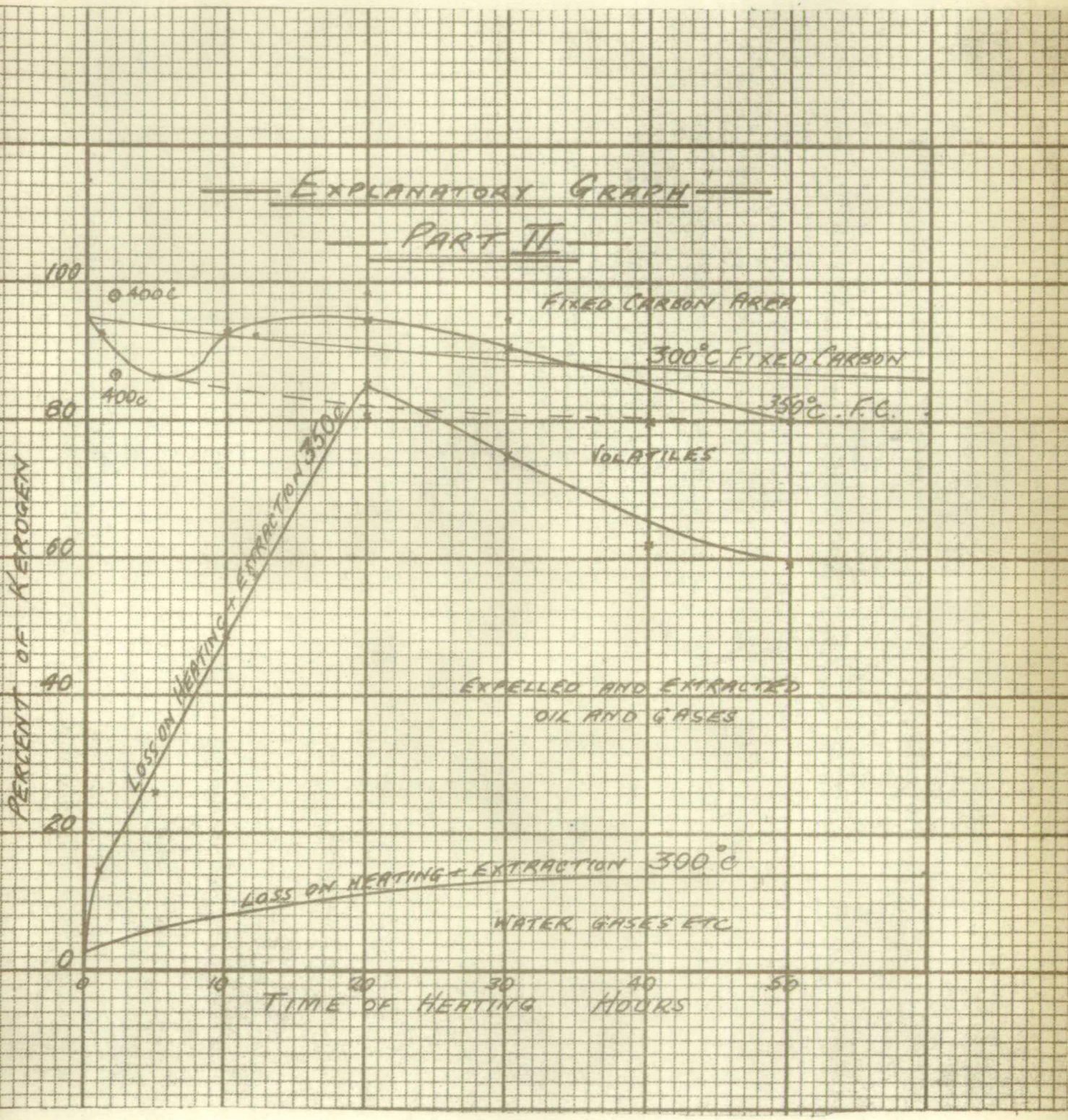
The hardness of the bitumen is about that of ~~of~~ an 80/100 penetration road bitumen.

The general results of this phase of the work confirms the soundness of the processes put forward for conversion of the kerogen into bitumen by heating the shale with heavy oils.

GENERAL CONCLUSIONS

It is often stated in the technical press concerning shale distillation that slow distillation is desirable. There are many known processes and operations where speed is detrimental to the finished product but all the evidence afforded by the work in this section leads to the belief that shale distillation is an exception.

Slow heating engenders changes in the kerogen material of Tasmanite resulting in the loss of oil and production of comparatively useless fixed carbon in the residue. The results are thus confirmatory of and supplementary to the work reported in Part III where it will be seen that oil production from a given size material ia a maximum for a relatively high rate of heating in the neighbourhood of 2 degrees Centigrade per minute.


EXPLANATORY GRAPH
PART II
100
80
60
40
20
0
PERCENT OF KEROGEN
400C
400c
FIXED CARBON AREA
300°C FIXED CARBON
350°C. F.C.
VOLATILES
LOSS ON HEATING + EXTRACTION 350°C
EXPELLED AND EXTRACTED
OIL AND GASES
LOSS ON HEATING + EXTRACTION 300°C
WATER GASES ETC
0
10
20
30
40
50
TIME OF HEATING HOURS

PART III

GENERAL INVESTIGATION OF TASMANITE OIL SHALE RETORTING.

The yield of a shale and the quality of the products obtained on distillation is influenced by the usual variables in retorting such as are enumerated in "Science and Industry" Vol. 2 No. 12, December 1920 page 754. The list of these variable factors somewhat expanded and enlarged is as follows:-

(a) Size of particle i.e. minimum dimension of particle

(b) Rate of rise of temperature of charge

(c) Time of contact of oil vapours with heated residue and surfaces.

(d) Effect of steam, carbon dioxide, hydrogen etc

(e) Effect of other solid substances in the charge

(f) Thickness of charge in retort

(g) Maximum temperature of distillation

(h) Pressure under which retorting takes place

(i) Variable efficiency of conversion of kerogen to oil with varying richness of shale.

In order to obtain information on these points in the case of Tasmanite a series of distillations were carried out on portions of one large sample of shale which was tolerably uniform in composition and by inter-comparison the effects of most of the above-mentioned variable factors could be obtained

NOTES ON THE SHALE SAMPLE USED IN THIS WORK.

It was considered at the time of commencing this work (1928) that if the shale industry was likely to be at all profitable, it would operate first on the richer shale. In the light of more recent knowledge, it may be profitable to retort the whole seam including the middle band which is generally much poorer in quality than the average rather than to attempt to sort out the band in the mine under disadvantageous conditions. Some 300 lbs. of shale representing as was supposed good average quality shale was obtained through the courtesy of Mr. Anderson of the Tasmanite Shale Oil Co. Subsequent work showed that this sample was richer than the average of the top and bottom seam even in the richer mine but not so much richer as to seriously affect any conclusions drawn.

This sample was coarsely crushed and thoroughly mixed and quartered down into several portions. The work carried out showed the sample to be homogeneous in ash content to the degree of 1% to give the extreme variations but the ash/shale ratio for most retortings showed very much closer approximation to the average value. When the pebbly nature of the shale and the variation in the various laminae of the seam are considered this must be regarded as satisfactory. If the shale could have been more finely crushed then greater homogeneity may have been realised but it was necessary to retain a moderately coarse particle size.

Work described elsewhere in this report showed that after sufficient drying at 100 C all moisture was expelled and no further loss in weight occurs till over 200 C. All retort charges were therefore dried to constant weight at 100 C.

Having taken the foregoing precautions to obtain retort charges uniform in composition within narrow limits it was possible to determine the influence of most of the factors enumerated above with the obvious exception of (i). For the determination of the factor (i) other samples of shale had to be distilled under definite conditions established from the work on the large standard sample.

EXPERIMENTAL RETORT USED

The experimental retortings were of the nature of large scale assays and it was considered that a charge of 1120 grams would be most convenient. If too large the work would be hinder ed in some respects while a sufficiently large charge was desirable to enable the chief characteristics of the oil to be determined with ease. With the above charge 5 m.l. of oil corresponds to one imperial gallon per ton of 2240 lbs

and as the oil could be computed to at least 1 m.l. the oil yield could be determined to at least 0.2 gallon per ton.

In order to utilise an existing heating furnace the maximum permissible internal diameter of the retort was 3.5 inches and by making it 15 inches long, 1120 grams of the richest shales could be retorted. For poor shales in the region of 90% ash 1.5 times this charge was used in some cases.

The retort was designed for use in the horizontal position and consisted of 15 inches of 3.5 inch steam pipe faced at each end and screwed with 12 threads per inch for a sufficient distance. Both ends were capped with steel caps of 4 inches external diameter and 1.5 inches long bored and screwed to fit the barrel. The ends were left 0.5" thick to provide ample metal for carrying the thermocouple tube and the several connections.

One cap carried at the centre a brass union for attachment of the 5/16" copper delivery pipe. The other cap carried at its centre a 3/8" internal diameter and 1/32" wall solid drawn steel tube projecting 7½" into the retort and with the inner end welded up gastight. This tube was chosen of steel and thin walled to lessen conduction of heat along it so that a thermocouple inserted into it with the hot junction in contact with the welded end would indicate the temperature of the centre of the charge. The same cap also had as near the tube as could be arranged a brass union for the attachment of a copper inlet tube for use when distilling in steam, hydrogen etc. In most of the work it was not required and the opening was closed with a special plug and union nut.

The joint between the cap and the barrel was made gastight by having the end of the barrel faced accurately plane and by having a solid copper ring of 1/8" thickness brazed into the cap and then faced off. Before screwing on the cap the joint surfaces were smeared with a paste of jeweller's rouge and shale oil residuum. On screwing up tightly a perfectly satisfactory joint was made which remained gastight through the distillation.

The sulphur compounds and especially the hydrogen sulphide attack the copper and after a few runs it becomes too pitted to use without refacing. In the later work the copper annular ring was replaced by a soft steel one which corroded only at about one tenth of the rate of the copper. The use of a standard copper-asbestos gasket was thus made possible and at the low pressures in question gave satisfaction. The copper sulphide formed by corrosion of the gasket could be removed from the face of the steel ring with a piece of unannealed copper tube and injury to the steel surface avoided. In like manner the barrel end could be stripped of copper sulphide and then faced with a few rubs of a sheet of very fine emery cloth

held on a piece of plate glass. Working in this way the same steel ring was used for about 30 distillations without refacing. The use of the rouge-oil paste to fill the minute corrosion pits was undoubtedly responsible for the maintenance of a satisfactory joint for this amount of work. No difficulty was experienced in removing the cap after a distillation provided the thread was moistened with eucalyptus oil or shale kerosene. A slight warming of the cap after the oiling was also an advantage making for still easier removal.

The temperature of the retort wall was obtained by inserting a thermojunction into a 1/8" diameter hole 1/8" deep, pening firmly in, and then lagging with asbestos cloth and pulp so as to obviate any direct radiation from the red hot wall of the heating furnace. These thermocouple wells were provided at intervals of 90 degrees round theretort and at 3 inch intervals longtitudinally but in all the runs only the centre one nearest to the welded end of the internal thermocouple tube and nearly in the same horizontal plane was used. Approximate heat conductivity data for crushed shale could be obtained by comparison of the readings of the two thermocouples at different rates of heating.

The heating furnace was a trifle over 4 inches internal diameter and 22 inches long in the wound part or heating section. The windings were spaced about 50% closer near the ends to allow somewhat for the greater heat loss from the ends of a furnace of this type. Plugs of insulating material were used to minimise the end heat loss and radiation and convection losses were reduced by a cover of bright tin plate. Both the cover and the plugs were removed in one or two runs to secure slow rise of temperature as satisfactory rheostats were not then available.

The removal of the end plugs would not cool the retort excessively as the end caps fitted snugly in the furnace and being in fairly close contact with the wall in the hotter portion would receive heat faster than the barrel which was approximately ¼" from the furnace wall and in no place in contact with it. In this way the tendency to cool retort ends was largely eliminated.

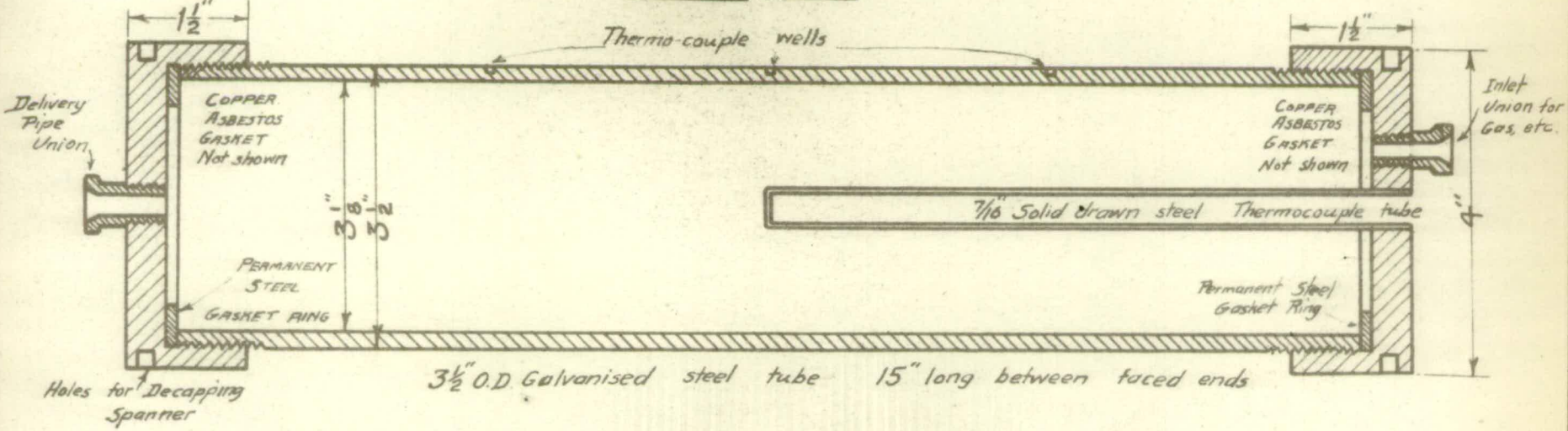
CONDENSING ARRANGEMENTS

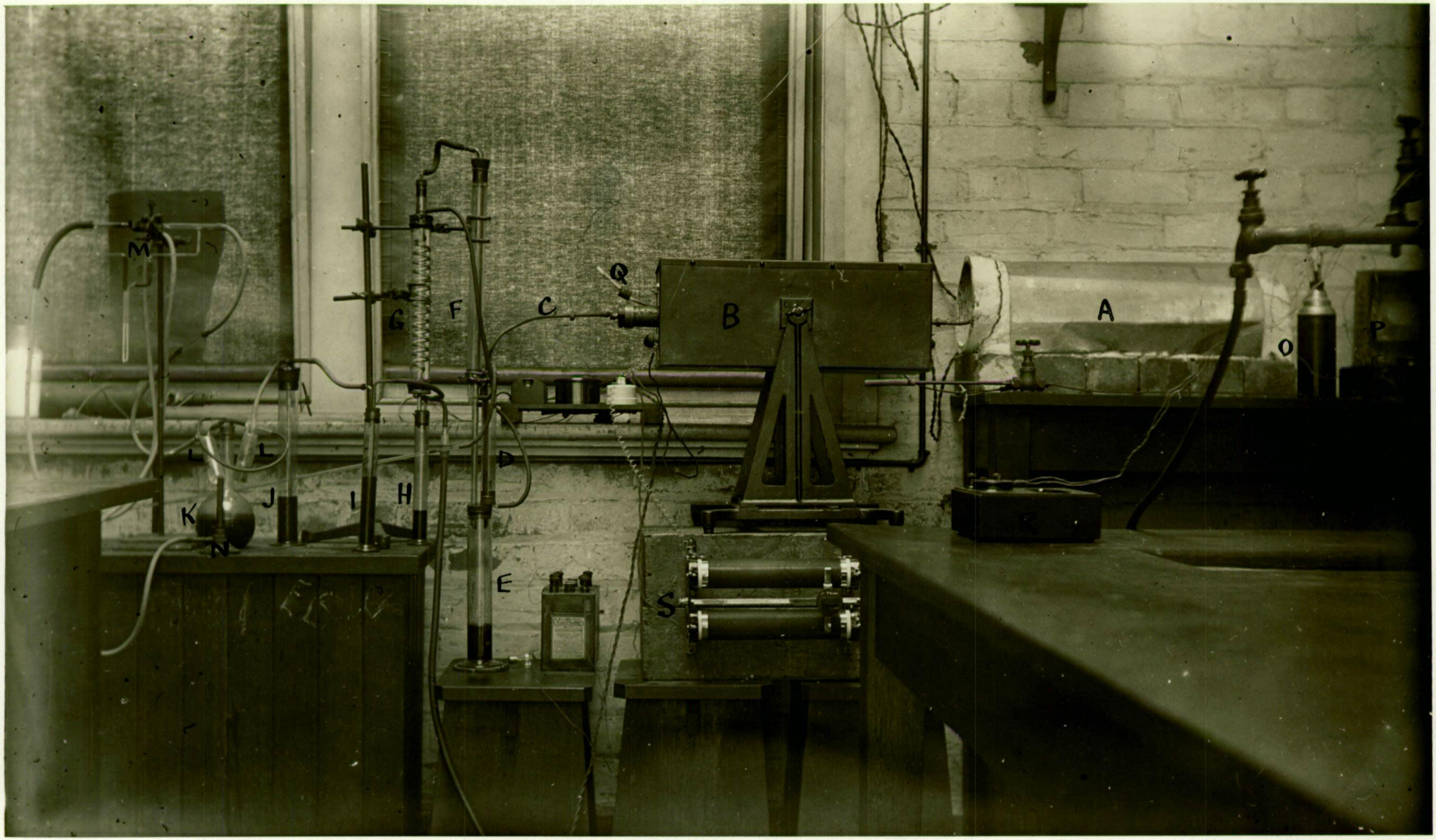
The preliminary work and especially Run No. 9 which is not reported showed conclusively that the condensing arrangements had to be ample and efficient if thorough condensation and separation of oil mist from the gas stream were to be effected.

PART III

SECTION OF RETORT

Scale ½ size





58.

The general assembly of apparatus for distillation is shown in the accompanying photograph. The principal parts are as follows:-

A. Retort heating furnace.

B. Electric furnace for heating the cracking tube.

C. Oil delivery pipe.

D. Water jacket on delivery pipe - first condenser.

E. First oil receiver.

F. Water jacket - second condenser.

G. Third condenser _ spiral oil mist separator.

H. Second oil receiver.

I. First oil scrubber.

J. Second oil scrubber.

K. Hydrogen sulphide scrubber.

L. Arnold absorption bulbs to complete hydrogen sulphide scrubbing.

M. Capillary flow meter.

N. Burner for burning the gas.

O. Thermos flask - cold end for retort thermocouples.

P. Microammeter for reading retort temperatures.

Q. Thermocouple for cracking tube temperatures.

R. Millivoltmeter for reading cracking tube temperature.

S. Regulating rheostat for cracking tube furnace.

Note. Furnace B shown in the photograph and containing the cracking tube was only used in Runs 30 to 33 inclusive. For all the other runs it was omitted and the oil delivery pipe C connected direct to the retort in furnace A.

It will be noticed that the oil vapours were delivered through a 5/16" copper tube water jacketed for a distance of 8 inches direct into a 500 m.l. graduated cylinder. Most of the condensation took place in this tube and as the crude oil from Tasmanite contains comparatively little paraffin wax no difficulty was experienced from choking or blocking of the relatively cool pipe. In order to gain head room and for further cooling the gases were led upwards through 24 inches of ⅜" diameter glass tubing water jacketed for more than half of its length and then downwards through a water jacketed worm of ¼" glass tubing having 10 turns of 1½"- 1⅝" diameter. The real purpose of the worm was to separate oil mist centrifugally as the gas entering the worm was already cooled to within a few degrees of water temperature. The cooling water was counter-current to the gas stream.

Any oil, condensed in the straight vertical tube dripped back into the first measuring cylinder while any oil separated by the worm dripped into a second and smaller measuring cylinder. It was only in the very fast distillations or in those distillations in a stream of permanent gas that there was any considerable part of the oil yield obtained in the second graduate. The photograph was taken after one of the cracking runs in which the large quantity of gas produced somewhat overloaded the first two condensers.

The progressive totals of the contents of both receiving cylinders could be read during a distillation and the progressive production of oil followed as in the accompanying graphs.

The gases were then bubbled through two measuring cylinders in series containing approximately 10 c.m. depth of an oil boiling over 300 C - Mobiloil E - or alternatively lighting kerosene of boiling range 200 C - 250 C to absorb low boiling hydrocarbons. Owing to its lesser viscosity and lower average molecular weight the kerosene was the more efficient but only to the extent of a fraction of a gallon per ton ona rich shale.

The gases were then passed through a wash bottle containing about 750 m.l. of 20% sodium hydroxide solution to absorb hydrogen sulphide and incidentally carbon dioxide. The absorption of hydrogen sulphide was quite quantitative provided a guard tube was used. Two Arnold absorption bulbs were used in series to ensure complete absorption of hydrogen sulphide and after a few runs it was found that one was quite sufficient for any traces of this gas which escaped the main absorber. The absorption of carbon dioxide was not quite as efficient as the absorption of hydrogen sulphide with the higher rates

of gas flow experienced.

The gas was then passed through a calibrated capillary flow meter to determine the gas yield from integration of the time-flow curve. The gas was then burnt though it would have been very desirable to have collected a sample each time for analysis. Owing to pressure of time and lack of essential apparatus no analyses nor determinations of calorific value could be carried out on the gas besides noting that it invariably burnt with a very luminous flame and nearly always contained sulphur compounds not removable by thorough alkali scrubbing. One rather crude determination of the calorific value of the alkali scrubbed gas in which no allowance was made for the inefficient absorption of heat and for radiation gave a value in excess of 500 B.Th.U. per cubic foot at N.T.P. It would seem that the gas has a high calorific value - this of course applying to simple distillation and not to distillation in steam.

In several of the first runs the hydrogen sulphide scrubber was omitted and sulphuric acid used to absorb ammonia. As the amount of ammonia formed during the oil production period was shown to be very small - less than 1 lb. ammonium sulphate per ton - it was not determined in all the later runs.

In one run the gases after oil scrubbing were passed through a freezing mixture at -19 C but only a drop or two of spirit condensed showing that to separate more spirit than the oil scrubbers absorbed, compression or similar methods would be necessary. The increase in volume of the absorber oil was therefore in following runs added to the measured oil yield to give the total distillation yield. On a few occasions more than two gallons per ton was obtained in the oil scrubbers but usually it was in the vicinity of one gallon per ton and with slow distillation still less.

OPERATION OF THE APPARATUS.

The general method of using the apparatus was as follows:- Somewhat ½ more than a charge of shale was dried to constant weight in a steam oven, the charge weighed out and put into the retort, the cap screwed on and the retort placed in the heating furnace. The various scrubbers being previously filled, all connections would then be made and the heating current switched on.

At suitable intervals readings were taken of retort wall temperature, internal temperature, water and oil levels in the first cylinder, oil level in the second cylinder, and the reading of the manometer of the capillary gas flow meter.

When distillation was complete as shown by absence of

further fluid distillate and slackening off of gas flow - gas continues to be evolved as long as the temperature is maintained or rises - , the heating current was cut off and the scrubbers disconnected to avoid sucking back.

The contents of the small receiver, if any, were then poured into the larger cylinder and allowed to stand some hours or overnight for settlement of water. The two levels were then read and the quantities of oil and water noted. In most of the work i.e. from Run 23 onwards the combined oil and water were also weighed and after pipetting off the oil the remaining one or two m.l. of oil were diluted with light petrol and dilute acid in measured quantity added to break greasy emulsions. After settlement and deduction of added acid the water could be accurately determined.

The oil yields in Runs 10 to 22 are thus perhaps in error due to low estimation of the water produced by counting the greasy emulsion, which is sometimes but not always produced, as oil. However as less than one gallon per ton is involved and there is a little uncertainty as to where to apply the correction the results for these runs have been left as originally recorded. The uncertainty arises because in some cases there was practically no emulsion so that on the whole in view of the smallness of the error it is better not to attempt to correct it.

In plotting the oil production curves the oil scrubber catches were added in with the progressive oil yield on a proportionate basis.

The retort when cool was disconnected, uncapped, the residue scraped out, weighed, crushed, and sampled.

The proximate analysis of the residue including sulphur, the specific gravity, sulphur content, saturation, and 100 m.l. distillation analysis of the oil were then determined. The amount of sulphur absorbed by the sodium hydroxide was determined on an aliquot portion. From this data a sulphur balance could be made showing the distribution of the original sulphur in the products of distillation.

From the weight of residue and its ash the ash content of the original shale charge could be checked and the amount of kerogen found by difference.

Division of the kerogen percentage in the dried shale into the oil yield in gallons per ton then gave the "Distillation Index" or factor of efficiency of distillation. The use of this index was introduced to give a convenient way of recording the efficiency of any distillation. The distillation index is that factor which multiplied by the percentage of kerogen in the dried shale will give the oil yield in gallons per ton.

More attention might have been paid to the nitrogen content of the oil as this is by no means inconsiderable. The clinging smell of Tasmanite shale oil is in large part due to basic

nitrogenous bodies but as these compounds are fairly readily removed by acid treatment the following of the distribution of nitrogen among the products of distillation was deliberately neglected on account of the amount of laboratory work involved, the performance of which would have further checked the progress of this single handed investigation which was already unavoidably slow.

Some idea of the relative accuracy of the various weighings and observations etc. may not be out of place.

Temperatures are subject to an error ofnot much more than one degree centigrade. The iron-constantan couples used were standardised at the boiling point of water, melting points of tin, lead, and zinc and a similar couple at the boiling pointof sulphur in sulphur vapour. The E.M.F.-temperature curve was very closely rectilinear and estimation to one degree was dependent on the splitting of a millimetre division on the scale into ten parts. This could be done without much more error than mentioned above. The galvanometer used was a Cambridge microammeter pattern "L" of over 600 ohms resistance and gave unqualified satisfaction throughout the whole of the work.

Water and oil yields except for the first few distillations were more closely measured and computed than indicated in the results sheets where they are generally given to the nearest 0.2 gallon per ton.

Specific gravities were determined by Westphal balance at room temperature which is very nearly 15 C during the part of the year in which the work was done. In spite of the viscosity of some of the oils the balance could be read to .001 though in the range just below 0.900 sp.gr. the balance was in error .002. In the range in which most of the oils fell the balance gave results accurate to .001.

Saturation percentages were obtained by mixing the crude oil with three volumes of 1.84 sp.gr. sulphuric acid and after thorough mixing and standing ten minutes, centrifuging until separation of paraffins was complete. Results could be duplicated to much closer than 2% and may be taken as accurate to about 1% of the original oil volume.

Sulphur determinations on the oil and shale were carried out by the sodium peroxide bomb method and the sodium peroxide used was of low sulphur content so as to give a reasonably low blank assay.

Residue sulphurs were determined by the Eschka method in an electric muffle and the precaution taken of acid treating the residue in order to obtain the real total sulphur. Both types of sulphur determination could be checked to at least 0.02%

The sulphur dissolved as hydrogen sulphide in the scrubber liquor was determined by evaporating an aliquot part and fusing with sodium peroxide. Some volatile sulphur compounds were perhaps lost here as the evaporating liqour smells fairly strongly of mercaptan like compounds but as hydrogen sulphide was really the chief interest these volatile compounds were allowed to appear in the gas and loss item in the sulphur balance. The term loss is used but practically all of this item is represented by sulphur compounds in the gas and not retained by sodium hydroxide owing to their chemical nature.

In some cases the scrubbed gas would be very sulphurous on combustion and in these cases usually about 10% of the sulphur in the shale would find its way into the gas.

The proximate analysis of the residue is given in each case having been determined on one gram in a covered platinum crucible with ignition temperature of 900 C to expel volatiles. The volatiles are shown separately from the fixed carbon but it is the total of these two that is perhaps the more important. In the case of rich shales there is an appreciable percentage of fixed carbon in the retort residue but with some poor shales the fixed carbon is nearly zero or may sometimes appear negative owing to gain in weight of the ignited residue by oxidation of mineral matter. The cause of this could not be always ascertained. Some samples of shale contain small amounts of arsenic which would partly account for the discrepancy between the ash content determined inthe two ways used.

With many samples of shale from different parts of the field, the ash determined on the retort residue in the course of the proximate analysis always gave consistent and somewhat lower results as compared with ignition of the same quantity in an open platinum basin with free access of air in an electric muffle at 600 C - 700 C. Formation of calcium sulphate from the carbonate was one explanation and this would take place more completely with full access of air. There are appreciable amounts of calcium sulphate in the shale before retorting so that this point was not to be settled without careful work. In addition the ash as determined in the open dish varies with the size of sample taken and further decreases appreciably on some hours ignition whereas the ash obtained in the course of the proximate analysis does not show this decrease. The ash obtained in the proximate analysis was therefore accepted as a working basis as the result could be quickly obtained and also be duplicated within narrow limits.

The ash determined in the open basin showed divergent results dependent on the quantity taken and therefore on the relative surface exposed and the length of time of ignition. Prolonged ignition for some hours at 800 C would bring the open basin ash down to the covered crucible value.

Ash/shale ratio is the calculated ash computed from the residue weight and ash as determined on the residue after crushing and mixing. All the weighings of the larger quantities were made to 0.5 gram and reported in most cases to the nearest gram. The ash/shale ratio is certainly closer to the true value than could be obtained from sampling the unretorted shale crushed to retorting size as the various laminae of the seam differ quite appreciably and the toughness of the rich shale makes the fines comparatively poor thus increasing sampling difficulties.

The indefinite term "kerogen" is used to denote throughout this work the difference between the shale dried to constant weight at 100 C and the ash as determined in the proximate analysis. It thus includes the organic matter in the shale, volatile substances such as part of the sulphur of pyrite and any arsenic sulphide, and combined water in the inorganic part of the shale. The latter item is small but the variable quantity of water produced in distillation compared with the oil makes it very probable that some is of mineral origin. This point is not absolutely certain because after drying the shale at 100 C thoroughly no additional water is expelled till well over 200 C. This observation is based on many different samples, at least 24 in number. It could be equally well explained by a slight variation in the hydroxyl part of the spore case material in different samples. It is, however, certain that a good part of the water is produced by the preliminary changes in the composition of the spore case material which precede the pyrolysis into bitumen.

The distillation index which is a quantity of use in the consideration of shale retorting has already been defined.

The rate of heating is an average rate of rise of temperature in the range 360 C - 480 C which may be regarded as the normal distillation range for Tasmanite oil shale.

The maximum rate of oil production is the rate in gallons of oil per ton per hour which holds while the distilling zone is advancing through the layer of shale in the retort. It is represented by the rectilinear portion of the oil production curve and for a given sample is the best measure of the speed of distillation.

The oil production time is given to the nearest 15 minutes except in the case of very fast distillations which are sharper in their commencemant and finish. Normally the oil comes over so slowly at the beginning and end that a ee closer measure of the time is not possible.

The scrubbed gas yield obtained from integration of the time-flow curve with a planimeter or by weighing the curve has been corrected for temperature and is given for N.T.P. conditions. The volumes of carbon dioxide and hydrogen sulphide are also given at N.T.P.

The eight products of distillation are shown as percentages of the original dried shale. These figures are given to the nearest .01% which is seldom justified but the second figure after the decimal point has been retained in order to make more accurate the expression of the products as percentages of the kerogen. These latter figures are rounded off to the nearest .05%.

All the computations in these distillation results have been made by a fairly accurately scaled ten inch slide rule which has an accuracy limit of 1 in 1000 so that errors not exceeding this magnitude may be found in several places but as the other determinations except weighings seldom approach this degree of accuracy such errors are not important. In many cases however the slide rule results have been checked at a later date by calculation.

SUMMARY OF DISTILLATIONS PERFORMED.

A summary of the distillations performed with the essential variations and the corresponding serial number of the run is as follows:-

Run No.	
10	Fast distillation of standard sample in flakes not exceeding ¼" thickness.
11	Slower distillation of standard sample in flakes not exceeding ¼" thickness. This run was interfered with by a heating power failure.
12	Distillation of standard sample in ¼" flakes in a current of carbon dioxide.
13	Distillation of standard sample in ¼" flakes in a current of superheated steam.
14	Repeat of Run No. 13. for checking purposes.
15	Repeat of Run No. 10 for checking purposes.
16	Distillation of standard sample in ¼" flakes in a current of hydrogen at atmospheric pressure.
17	Distillation of standard sample in ¼" flakes with addition to the charge of 10% pulverised limestone.
18	Distillation of standard sample in ¼" flakes with addition to the charge of 10% pulverised quicklime.
19	Slow distillation as a check on Run No. 11 to exclude the effect of the power failure.
20	Slow distillation of standard sample crushed through a 20 mesh screen. "Fractional eduction" tested out also.
21	Faster distillation of standard sample crushed through 20 mesh.
22	Fast distillation of standard sample in pieces of minimum thickness ½ inch.
23	Conditions as in Run No. 10 for checking purposes and to measure gas yield.

24 Very fast distillation of standard sample in flakes not exceeding 3/16" thickness.

25 Very fast distillation of standard sample in pieces of ¾" - 1" thickness.

26 Very slow distillation of standard sample in 3/16" flakes.

27 Distillation of standard sample crushed to -20 mesh but faster than Run 21.

28 Distillation of standard sample in 3/16" flakes but somewhat faster than Run 24.

29 Distillation of standard sample in ½" thickness flakes with little fines and faster than Run 22.

30 Distillation of standard sample 3/16" flakes but with the vapours passed through a cracking tube packed with shale residue and maintained at 700 C to 800 C.

31 Distillation of standard sample 3/16" flakes and with the vapours passed through a cracking tube packed with copper turnings and maintained at approx. 700 C.

32 Distillation of standard sample 3/16" flakes and with the vapours passed through a cracking tube packed with shale residue and maintained at approx. 460 C.

33 Distillation of standard sample 3/16" flakes and with the vapours passed through a cracking tube packed with shale residue and maintained at approx. 560 C.

34 Distillation of a sample of shale obtained from the Australian Shale Oil Corporation. Ash 79.9%, in ¼" thickness flakes, rate of heating 95 C per hour.

35 Distillation of a sample of middle band from the Tasmanite Shale Oil Co., ash 90.6%, rate of heating 80 C per hour.

36 Distillation of a sample of very poor middle band from the Tasmanite Shale Oil Co., ash 93.5%, rate of heating 85 degrees Centigrade per hour.

37 Distillation of a sample of retort feed to"Long" retort, Tasmanite Shale Oil Co., ash 68.3%, rate of heating 80 deg. C per hour.

38 Distillation of richest shale obtainable from the Tasmanite Shale Oil Co., ash 61.9%, in ¼" flakes, rate of heating 80 dg. C per hour.

39 Distillation of survey sample 8A, bottom seam, ash 83.5%, rate of heating 80 C per hour.

40 Distillation of survey sample 8B, middle band, ash 84.75%, rate of heating 80 C per hour.

41 Distillation of survey sample 8C, top seam, ash 70.0%, rate of heating 70 C per hour.

42 Distillation of survey sample 3A, bottom seam, ash 75.3%, rate of heating 65 C per hour

43 Distillation of survey sample 14A, bottom seam, ash 81.7%, rate of heating 95 deg.C per hour.

44 Distillation of survey sample 18A, bottom seam, ash 77.5%, rate of heating 100 deg.C per hour.

45 Distillation of survey sample 10B, middle band, ash 89.3%, rate of heating 95 deg.C per hour.

46 Distillation of survey sample 20B, middle band, ash 89.8%, rate of heating 105 deg.C per hour.

47 Distillation of survey sample 6C, top seam, ash 71.6%, rate of heating 105 deg.C per hour.

48 Distillation of survey sample 19C, top seam, ash 80.2%, rate of heating 110 deg. C per hour.

49 Distillation of standard sample in ¼" flakes, rate of heating 100 deg.C per hour and under one sixth atmosphere pressure.

50 Distillation of survey sample 19C, ash 79.7%, rate of heating 100 deg.C per hour and under absolute pressure of approximately one seventh atmosphere.

51 Distillation of sample from Tasmanite Shale Oil, Co., to correlate Crozier retort operation, ash 71.3%, rate of heating 100 deg.C per hour, particle size ¼" minimum dimension.

52 Distillation of standard sample in ¼" flakes, ash 67.1% in a current of steam and at a rate of heating of 35 deg.C per hour to see how much of the discrepancy between the yields on slow and fast distillation could be recovered by ample steaming.

53 Distillation of standard sample in ¼" flakes, ash 67.2% very slowly with the p temperature practically constant at 410 C for 50 hours.

54 Distillation of rich spore material concentrate obtained by separating pulverised shale in 1.32 sp.gr. ferrous chloride solution, ash 24.3%, rate of heating 115 deg.C per hour.

55 Distillation of the tailings from the ferrous chloride separation, ash 78.9%, rate of heating 85 deg.C per hour.

56 Distillation of sample of shale from Tasmanite Shale Oil Co. to correlate operation of Crozier retort. Ash 71.7%, in ¼" flakes, rate of heating 70 deg.C per hour.

57 Distillation of spore-free material obtained by separating the pulverised standard sample in carbon tetrachloride. Ash 85.5%, rate of heating 65 deg.C/hour.

58 Distillation of sample from Tasmanite Shale Oil Co to correlate operation of Crozier retort. The sample consisted of the whole seam as mined in the Goliath mine, new tunnel, ash 80.4%, rate of heating 70 deg.C per hour.

59 Distillation of standard sample in ¼" flakes, ash 66.2% and under low absolute pressure, approximately one fifth atmosphere. Rate of heating 27 deg.C per hour.

60 Distillation of standard sample in ¼" flakes, ash 66.1%, and under low absolute pressure, approximately one fifth atmosphere. Rate of heating 60 deg.C per hour.

All the essential data relating to these distillations will be found in the tabulated results sheets which show practically all the quantitative data obtained in each run together with certain calculated quantities such as distillation index.

The full details of each run are given under their separate headings. All the data and figures to be found in the tabulated results sheets are given together with the observations of time, temperatures, progressive oil production, gas flow, and other relevant data.

The percentage distribution by weight of the various products of distillation and the further expression of these excluding the ash, on an ash-free basis will be found in both sets of figures. The gravimetric efficiency of distillation is thus available for ready comparison.

In the discussion of the influence of the various factors referred to at the commencement of Part III it will be sufficient to quote the number of the run or distillation...

RUN No. 10

Charge 1205 grams standard sample 66.6% ash in ¼" flakes.
Ammonia collected in sulphuric acid. Room temperature 12 C.
Switched on 2 heats at 2.15 p.m.
Oil scrubber catch 4.5 m.l. Gas passed through a U-tube immersed in a freezing mixture at -19 C subsequent to ammonia scrubbing.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	REMARKS
2.30	67	23		
2.45	145	50		
3.00	218	100		Water over
3.10	268	135		at 3.07
3.20	304	171		
3.30	340	213		Traces oil
3.40	373	263	0.2	
3.50	400	302	0.9	
4.00	429	341	2.8	Gas burns
4.10	450	373	7.4	at 4.03
4.20	469	412	19.0	
4.30	488	422	32.6	
4.40	504	439	44.8	
4.50	523	476	50.3	
5.00	538	506	52.1	
5.10	554	526	52.6	
5.20	572	544	53.0	
5.30	580	559	53.0	
7.30			53.0	

Oil yield gallons per ton	53.0
Water do.	5.0
Specific gravity of oil 15 C	0.925
Sulphur content of oil	2.47%
Saturation not determined	

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	11.4%
150 to 200	9.7%
200 to 250	11.0%
250 to 300	12.6%
Residuum	55.3%

Residue weight	881 grams
Residue expressed as percentage of shale	73.05

Proximate Analysis of residue.

Volatiles at 900 C 4.6% Fixed Carbon 4.35% Ash 91.05% Sulphur 1.7

RUN No. 10 continued.

Sulphur distribution

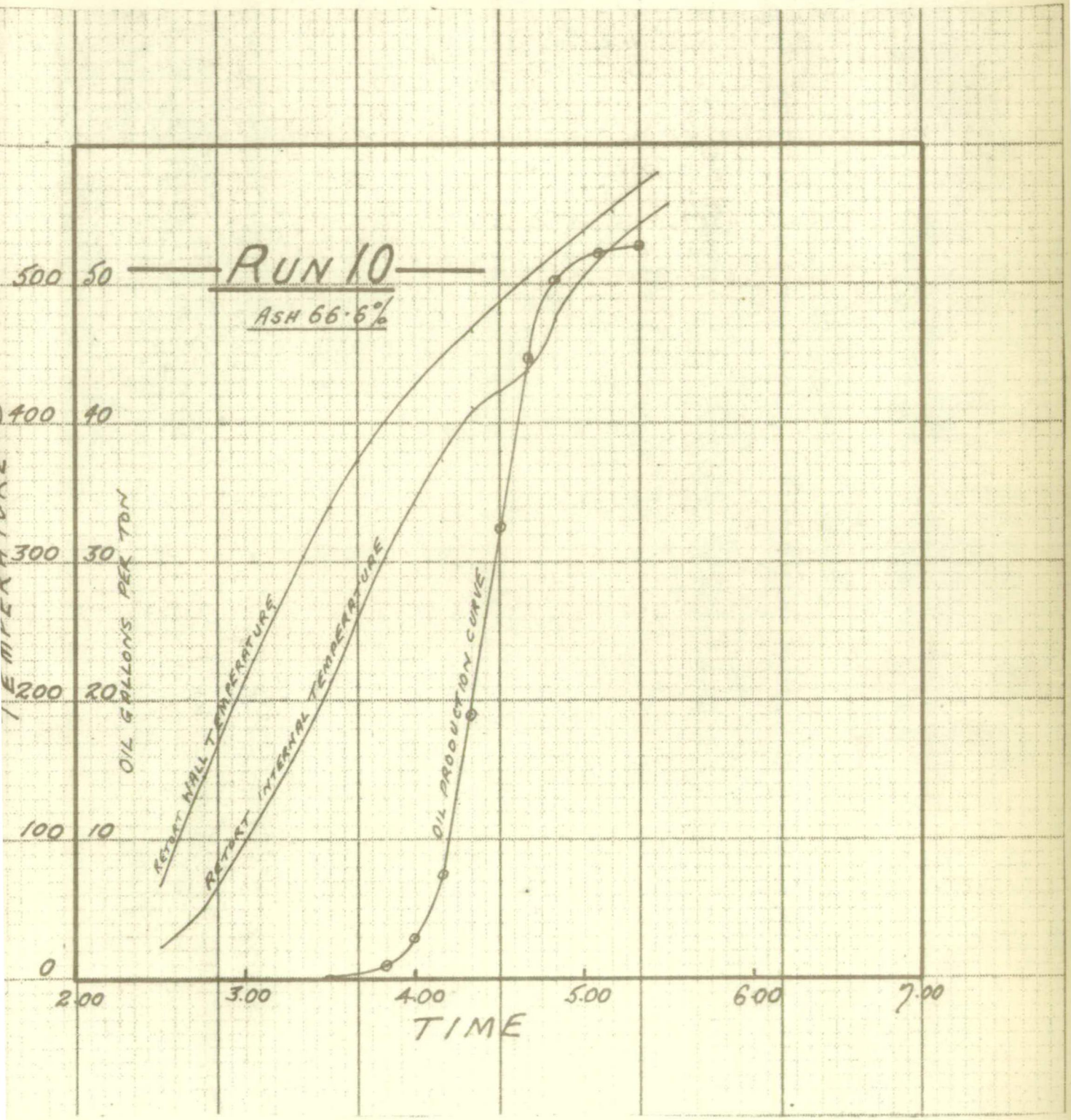
Residue 48.1% Oil 20.5%

General Data.

Ash/shale ratio	0.666
Kerogen percentage	33.4%
Distillation Index	1.58
Rate of heating in distillation range	140 degrees/hour
Total time of oil production	1.5 hours
Maximum rate of oil production	72 galls/ton/hour
Ammonia yield as sulphate	1.14 lbs. per ton

Weight Balance on Products of Distillation.

	Percent of shale	Ashless basis
Ash	66.6%	
Volatiles in residue	3.36	10.05%
Fixed carbon in residue	3.18	0.50
Oil	21.88	65.55
Water	2.23	6.65
Gases and loss.	2.75	8.25
	100.0	100.0


RUN 10
ASH 66·6%
500
400
300
200
100
0
50
40
30
20
10
OIL GALLONS PER TON
RETORT WALL TEMPERATURE
RETORT INTERNAL TEMPERATURE
OIL PRODUCTION CURVE
2.00
3.00
4.00
5.00
6.00
7.00
TIME

RUN No. 11

Charge 1120 grams standard sample ash 66.6% in ¼" flakes.
Ammonia collected in sulphuric acid.
Switched on one heat at 11.15 a.m. Power supply failed about 3.30 p.m. Switched on two heats at 3.53 p.m. and cut back to one heat at 4.20 p.m.
Oil scrubber catch 1 m.l.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	REMARKS
11.30	35	21		
12.00	104	48		
12.30	178	114		
1.00	244	178		
1.30	295	249		
2.00	336	301		
2.07	346	314	1.0	
2.30	372	347	1.4	
2.45	383	363	2.0	
3.00	395	379	3.2	
3.15	406	392	5.6	
3.30	395	399	9.0	
3.45	382	395	10.2	
4.00	390	388		
4 .15	422	397	12.4	
4.30	447	414	19.0	
4.45	456	431	31.0	
5.00	464	446	38.0	
5.15	472	462	42.8	
5.30	480	473	45.4	
7.00	520	518	48.0	

Water gallons per ton	5.0
Oil Yield gallons per ton	48.0
Specific gravity of oil	0.905
Sulphur content of oil	2.43%
Saturation of oil not determined	

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	14.7%
150 to 200	10.3
200 to 250	10.5
250 to 300	12.5
Residuum	52.0

Residue

Weight 836 grams Percentage of shale 74.6

Run No. 11 continued

Proximate Analysis of residue

Volatiles 5.60% Fixed carbon 5.20% Ash 89.2% Sulphur 1.73%

Sulphur distribution in products.

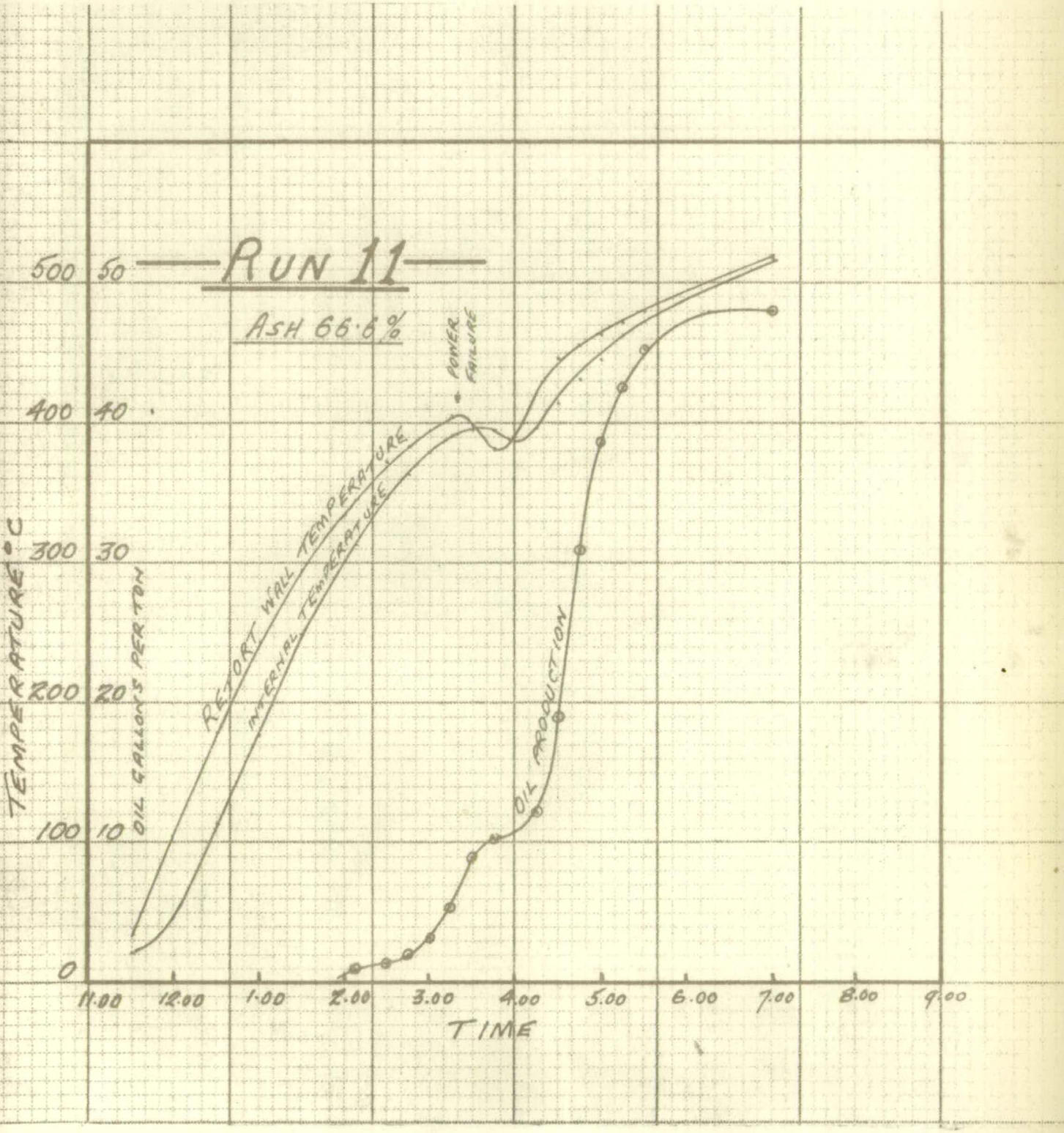
Residue 49.7% Oil 18.4%

General Data

Ash/shale ratio	0.666	
Kerogen percentage	33.4	
Distillation Index	1.44	
Rate of heating in distillation range	50	degrees/hour
Total time of oil production	5	hours
Maximum rate of oil production	52	galls/ton/hour
Maximum rate of oil production/% kerogen	1.56	do.
Ammonium sulphate yield	0.7	lbs per ton

Weight Balance on products of distillation.

	Percentage of shale	On ashless basis
Ash	66.6	
Volatiles in residue	4.18	12.50%
Fixed carbon in residue	3.88	11.60
Oil	19.38	58.05
Water	2.23	6.7
Gases and loss.	3.73	11.15
	100.0	100.0


RUN 11
ASH 66·6%
POWER FAILURE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
500
400
300
200
100
0
50
40
30
20
10
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
TIME

RUN No. 12

Charge 1120 grams standard sample 66.8% ash in ¼" flakes.
Ammonia not collected. carbon dioxide
Distilled in a current of ~~steam~~ preheated to approximately 200 C before entering retort.
Switched on one heat at 12.00 noon, changed to two heats at 2.40
Cut back to one heat at 4.30
Carbon dioxide started at 2.40 p.m.
Oil scrubber catch 12 m.l. or 2.4 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	CARBON DIOXIDE LITRES/HOUR
12.50	105	41		
2.40	316	270		
2.50	335	286	0.4	
3.00	360	300	0.6	
3.11	393	322	1.0	
3.20	415	343	1.5	45
3.30	440	370	4.2	
3.40	456	394	9.6	55
3.50	474	410	22.0	56
4.00	491	426	35.8	57
4.10	509	443	45.0	53
4.20	525	472	47.8	50.5
4.30	543	501	48.6	50.5
4.40	550	522	49.0	
5.00	546	538	49.6	57.0

Water produced gallons per ton	5.0
Oil yield gallons per ton	49.6
Specific gravity of oil	0.945
Sulphur content of oil	2.30%
Saturation of oil not determined	

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	9.8%
150 to 200	10.0
200 to 250	11.3
250 to 300	12.7
Residuum	56.2

Residue

Weight 824 grams Percentage of shale 73.6%

Proximate Analysis of residue

Volatiles 3.95% Fixed carbon 5.10% Ash 90.95% Sulphur 1.92%

Run No. 12 continued

Sulphur distribution in products

Residue 54.3% Oil 18.2%

General Data

Ash/shale ratio	0.668	
Kerogen percentage	33.2	
Distillation Index	1.50?	
Rate of heating in distillation range	120	degrees/hour
Total time of oil production	2	hours
Maximum rate of oil production	80	galls/ton/hour
do. per % kerogen	2.40	

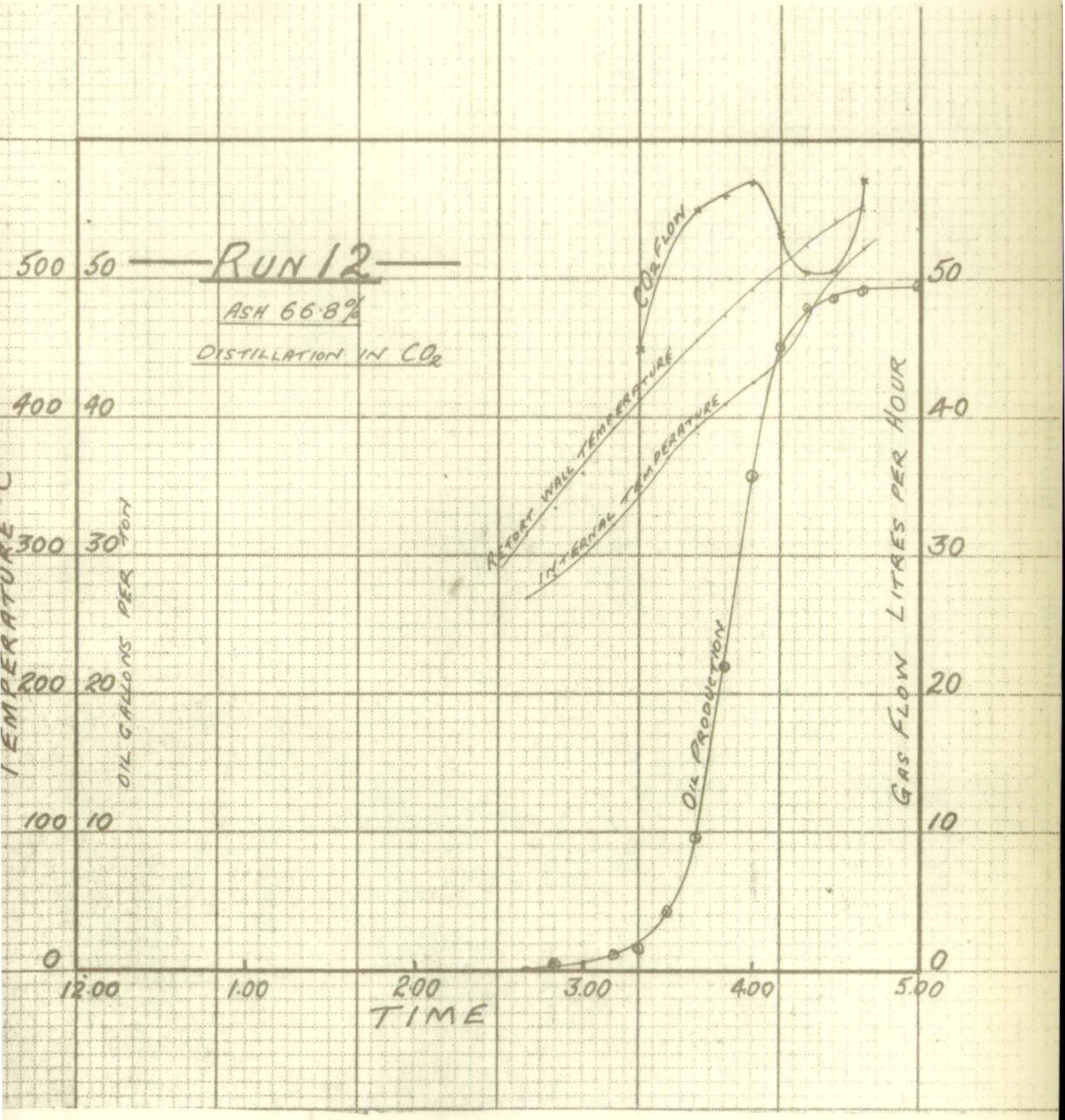
Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.8	
Volatiles in residue	2.90	8.70
Fixed carbon in residue	3.75	11.30
Oil	20.90	63.00
Water	2.23	6.70
Gases and loss	3.42	10.30
	100.0	100.0

General Note

It is considered that one to two gallons of oil per ton remained uncondensed owing to the lessening of the partial pressure of the lighter oil vapours by dilution with carbon dioxide.

This run is worthy of comparison with Run 49 - a reduced pressure distillation on a similar sample of shale. Much the same results are achieved by lowering the partial pressure of the oil vapours in the two ways and in both cases condensation difficulties are enhanced.


RUN 12
ASH 66·8%
DISTILLATION IN CO_2
CO_2 FLOW
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
12·00
1·00
2·00
3·00
4·00
5·00

RUN No. 13

Charge 1120 grams standard sample, 66.6% ash in ¼" flakes.
Ammonia collected in sulphuric acid.
Distilled in a current of steam superheated to approximately 200 C.
Switched on one heat at 5.20 p.m. changed to two heats 7.05 p.m.
No progressive figures of oil yield were determinable as the oil and water condensing together formed some emulsion which separated too slowly to read the interface.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE
7.05	270	191
7.15	298	222
7.30	352	270
7.45	396	312
8.00	434	331
8.15	465	400
8.32	498	440
8.45	523	473
9.00	545	523

Distillation was completely finished at 9.00 p.m.

Oil yield gallons per ton	51.2
Specific gravity of oil	0.952
Sulphur content of oil	2.38%
Saturation of oil	14%

Distillation Analysis of crude oil 100 m.l. computed

Up to 150 C	12.0%
150 to 200	7.5
200 to 250	10.8
250 to 300	13.1
Resduum	56.6

Residue

Weight 824 grams Percentage of shale 73.6%

Proximate Analysis of residue

Volatiles 5.45% Fixed carbon 4.0% Ash 90.55% Sulphur 1.70%

Sulphur distribution in products

Residue 48.0% Oil 19.7%

Run No. 13 continued

General Data

Ash/shale ratio	0.666
Kerogen percentage	33.4%
Distillation index	1.53
Rate of heating in Distillation range	140 deg. C/hour
Total time of oil production	1.5 hours
Ammonium sulphate yield	1.61 lbs/ton
Steam used expressed in gallons water/ton	40 galls/ton

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.6	
Volatiles in residue	4.0	12.0
Fixed carbon in residue	2.95	8.85
Oil	21.75	65.05
Water, gases, and loss	4.7	14.1
	100.0	100.0

General Note

This run had certain unsatisfactory features e.g. steam flow was irregular and rather deficient towards the end of the distillation. Some scrubber oil was sucked back into ~~of~~ the condensate in the receiver under the spiral condenser and though the oil recovery was not thereby rendered inaccurate as regards volume, distillation had to be resorted to for separation of the oil and the distillation analysis of the total crude had to be computed.

It was also noticed that caking of the residue was more pronounced in this run.

RUN No. 14

Charge 1120 grams standard sample, 66.8% ash, in ¼" flakes.
Ammonia yield determined.
Distilled in a current of steam superheated to approximately 200 C.
Oil scrubber catch 4 m.l. = 0.8 gallon per ton.
Switched one heat 1.15 p.m., two heats 2.50, cut back to one heat at 5.00, off 5.15 p.m.
No progrssive figures were determinable owing to the difficulty of reading the oil-water interface.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE
2.55	238	147
3.15	308	199
3.30	357	250
3.45	403	305
4.00	439	356
4.15	467	397
4.30	492	425
4.45	514	457
5.00	544	508
5.15	548	533

Oil yield gallons per ton	51.8
Specific gravity of oil	0.952
Sulphur content of oil	2.61
Saturation of oil	14%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	11.1%
150 to 200	7.8
200 to 250	9.7
250 to 300	11.4
Residuum	60.0
	100.0

Residue

Weight 824 grams Percentage of shale 73.6%

Proximate Analysis of residue

Volatiles 5.3% Fixed carbon 3.8% Ash 90.9% Sulphur 1.70%

Sulphur distribution in productd

Resdue 48.1% Oil 22.0%

Run No. 14 continued

General Data

Ash/shale ratio	0.668
Kerogen percentage	33.2%
Distillation Index	1.56
Rate of heating in distillation range	120 deg.C/hour
Total time of oil production	1.5 hours
Ammonium sulphate yield	1.8 lbs/ton
Steam used expressed in gallons of water/ton	40 galls/ton

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.8%	11.75%
Volatiles in residue	3.90	
Fixed carbon in residue	2.80	8.45
Oil	22.0	66.25
Water, gases, and loss	4.5	13.55
	100.0	100.0

General Note

This run was satisfactory in all respects and the steam flow was uniform throughout the distillation as it was electrically generated and therefore constant. The amount of steam used was only about half that used in the Scottish practice but the results may be taken to represent reasonably well fast distillation in excess of steam.

Caking of the residue was again more pronounced than in simple distillation.

RUN No. 15

Charge 1120 grams standard sample, 66.5% ash, in ¼" flakes.
This run was carried out to compare simple fast distillation with the last four runs and to serve as a duplicate of Run 10 except in quantity used.
Switched on two heats at 1.00 p.m., cut back to one heat at 3.40 and switched off at 4.00 p.m.
Ammonia not collected in this run.
Hydrogen sulphide absorbed from gas stream in sodium hydroxide solution.
Oil scrubber catch 5 m.l. = 1.0 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLS/TON
1.30	127	39	
2.00	295	153	
2.15	345	216	0.6
2.30	393	288	1.0
2.45	437	358	3.0
3.00	467	404	16.0
3.15	496	434	38.2
3.30	525	483	50.6
3.45	548	526	52.6
4.00	549	546	52.6

Water gallons per ton	4.6
Oil yield gallons per ton	52.6
Specific gravity of oil	0.925
Sulphur content of oil	2.40%
Saturation of oil	26%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	11.1%
150 to 200	10.7
200 to 250	9.6
250 to 300	12.7
Residuum	55.9
	100.0

Residue

Weight 816.5 grams Percentage of shale 72.9%

Proximate Analysis of residue

Volatiles 4.6% Fixed carbon 4.25% Ash 91.15% Sulphur 1.65%

Run No. 145 continued

Sulphur distribution in products of distillation

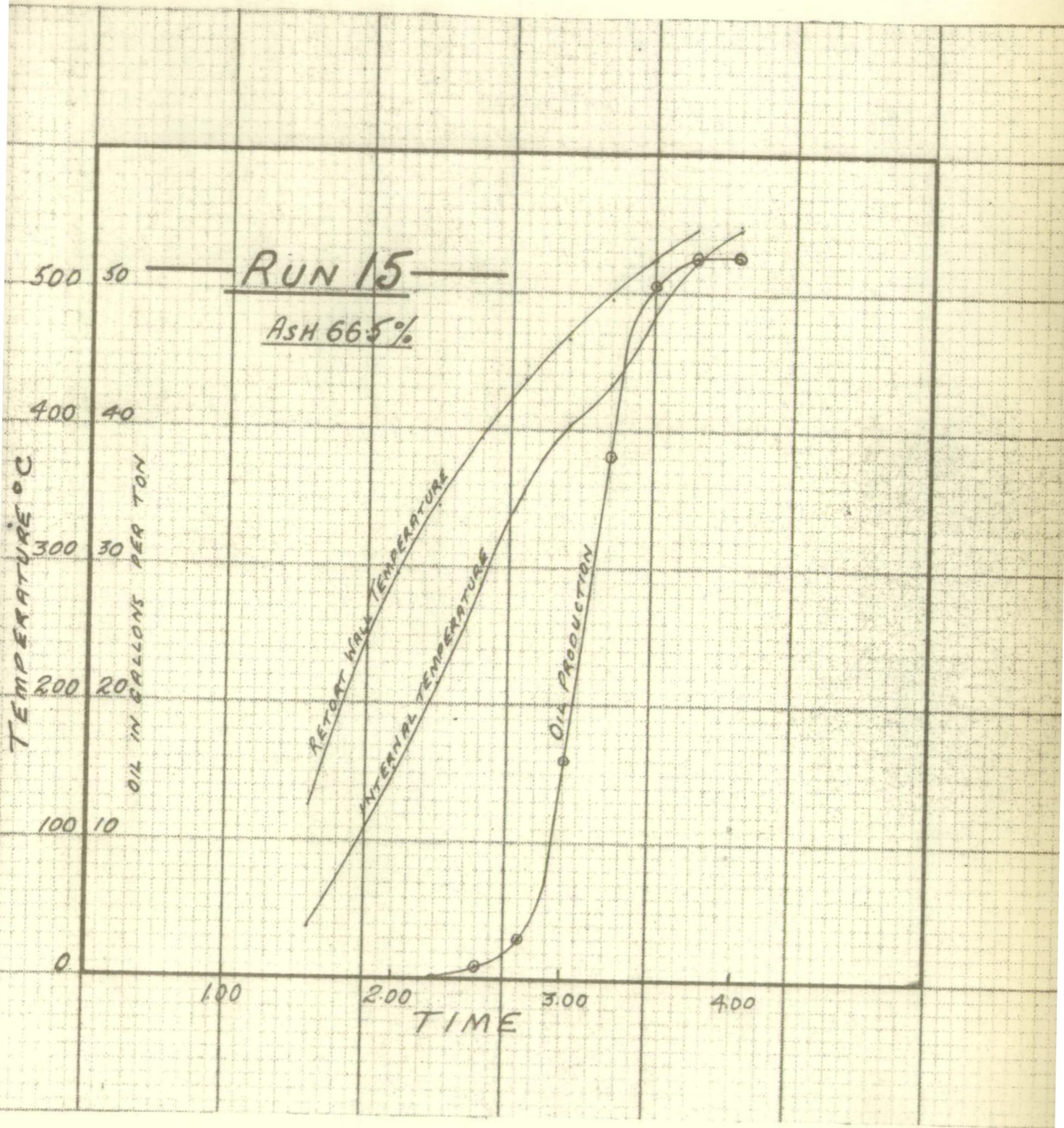
Residue	46.3%
Oil	19.9%
Hydrogen sulphide	30.0%
Other gases & loss	3.8%
	100.0

General Data

Ash/shale ratio		0.665	
Kerogen percentage		33.5%	
Distillation Index		1.57	
Rate of heating in distillation range		170	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		90	galls/ton/hour
do. per per cent kerogen		2.69	do.
Gas production	carbon dioxide	44	cu.ft./ton
	hydrogen sulphide	~~147~~ 156	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.50%	
Volatiles in residue	3.36	10.00%
Fixed carbon in residue	3.10	9.25
Oil	21.72	64.90
Water	2.05	6.10
Carbon dioxide	0.24	0.70
Hydrogen sulphide	0.62	1.85
Other gases and loss	2.41	7.20
	100.00	100.00


RUN 15
ASH 66.5%
TEMPERATURE °C
OIL IN GALLONS PER TON
500
400
300
200
100
0
50
40
30
20
10
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
1.00
2.00
3.00
4.00
TIME

RUN No. 16

Charge 1120 grams standard sample, 66.5% ash, in ¼" flakes.
Distilled in a current of hydrogen at atmospheric pressure.
Switched on two heats at 1.45 p.m., cut back to one heat at 4.53.
Two oil scrubbers used for the first time.
Oil scrubber catches 6 and 2 m.l. respectively = 1.6 gallons/ton.
Ammonia not collected in this and subsequent runs.
Gas scrubbed to remove hydrogen sulphide.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	HYDROGEN FLOW LITRES/HOUR
2.15	100	30		
2.30	180	83		
2.45	249	135		
3.00	310	192		
3.15	362	276		
3.30	400	332	1.0	
3.45	440	376	4.2	31
4.00	466	410	19.0	38
4.07				60
4.15	493	436	39.6	53
4.30	516	476	49.0	43
4.45	540	524	52.0	38
5.00	549	545	52.4	

Water condensed gallons per ton	&	4.0
Oil yield gallons per ton		52.4
Specific gravity of oil		0.930
Sulphur content of oil		2.31%
Saturation of oil		22%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	8.4%
150 to 200	10.7
200 to 250	10.8
250 to 300	11.7
Residuum	58.4
	100.0

Residue

Weight 812 grams Percentage of shale 72.5%

Proximate Analysis of residue

Volatiles 4.0% Fixed carbon 4.2% Ash 91.8% Sulphur 1.79%

Run No. 16 continued

Sulphur distribution in products of distillation

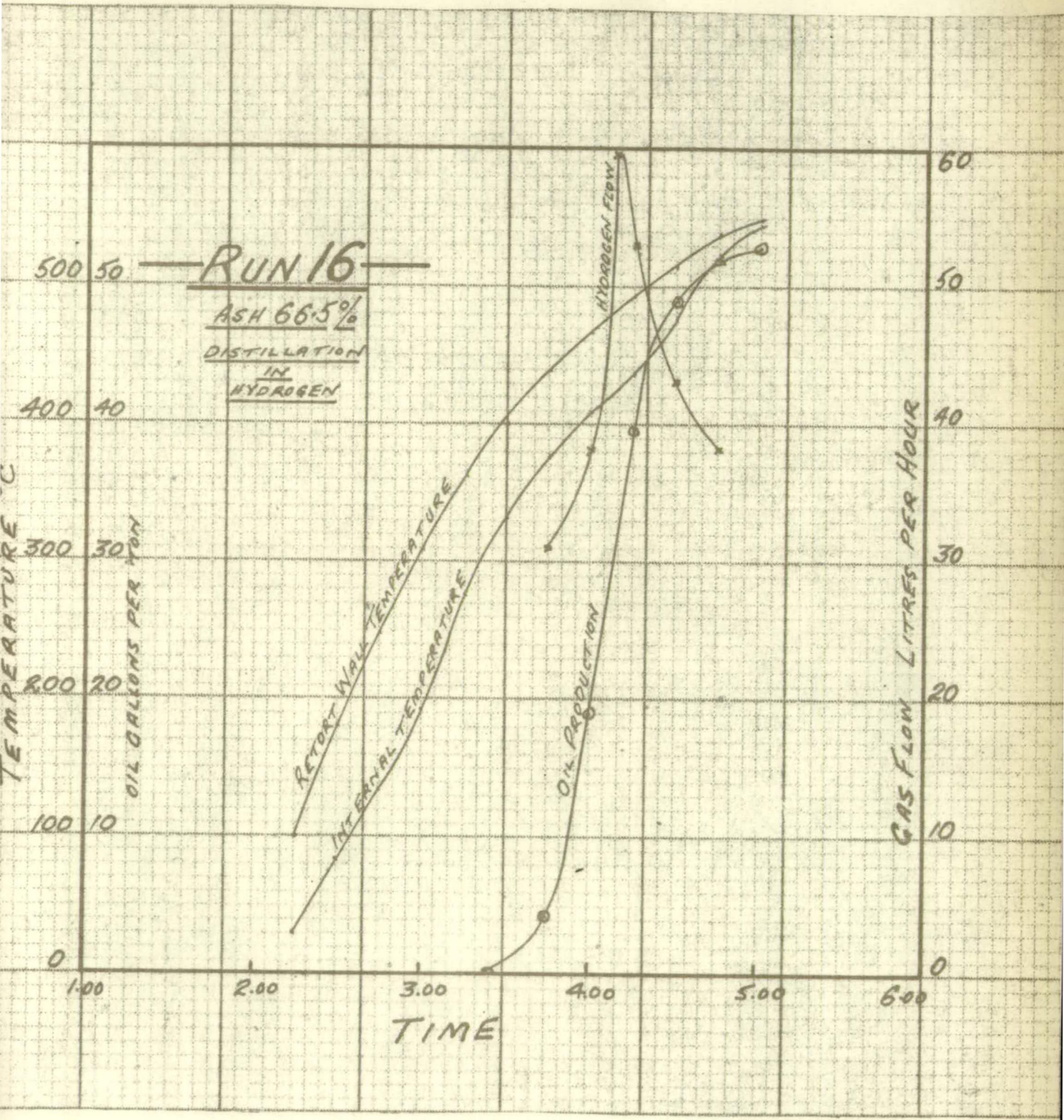
Residue	50.0%
Oil	19.5
Hydrogen sulphide	26.8
Other gases and loss	3.7
	100.0

General Data

Ash/shale ratio	0.665	
Kerogen percentage	33.5%	
Distillation Index	1.57	
Rate of heating in distillation range	140	deg.C/hour
Total time of oil production	1.5	hours
Maximum rate of oil production	80	galls/ton/hour
do. per % kerogen	2.38	do.
Gas production carbon dioxide	77	cu.ft./ton
hydrogen sulphide	185	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.50	
Volatiles in residue	2.90	8.65%
Fixed carbon in residue	3.05	9.10
Oil	21.72	64.85
Water	1.78	5.30
Carbon dioxide	0.42	1.25
Hydrogen sulphide	0.78	2.35
Other gases and loss	2.85	8.50
	100.00	100.00


RUN 16
ASH 66.5%
DISTILLATION IN HYDROGEN
HYDROGEN FLOW
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
60
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 17

Charge 1120 grams standard sample, 66.5% ash, in ½" thickness flakes mixed with 112 grams finely pulverised Ida Bay limestone assaying 96% calcium carbonate.
Switched on two heats 2.10 p.m., cut back to one heat at 5.00 p.m.
Gas scrubbed to remove hydrogen sulphide.
Oil scrubber catches 3 m.l. and 1 m.l. = 0.8 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON
2.30	69	12	
2.45	142	47	
3.00	219	98	
3.15	290	161	
3.30	341	231	0.2
3.45	393	300	1.0
4.00	430	363	3.6
4.15	460	405	13.2
4.30	490	434	34.8
4.45	514	473	45.6
5.00	540	520	49.0
5.15	548	542	50.0

Water condensed gallons per ton	5.4
Oil yield gallons per ton	50.0
Specific gravity of oil	0.926
Sulphur content of oil	2.36%
Saturation of oil	27%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	12.3%
150 to 200	10.2
200 to 250	10.8
250 to 300	14.1
Residuum by difference	52.6
	100.0

Residue

Nett weight less limestone 823 grams Percentage of shale 73.5%

Proximate Analysis of residue not determined

Run No. 17 continued

Sulphur distribution in products of distillation

Residue	45.0%
Oil	18.5
Hydrogen sulphide	26.7
Other gases and loss	9.8
	100.0

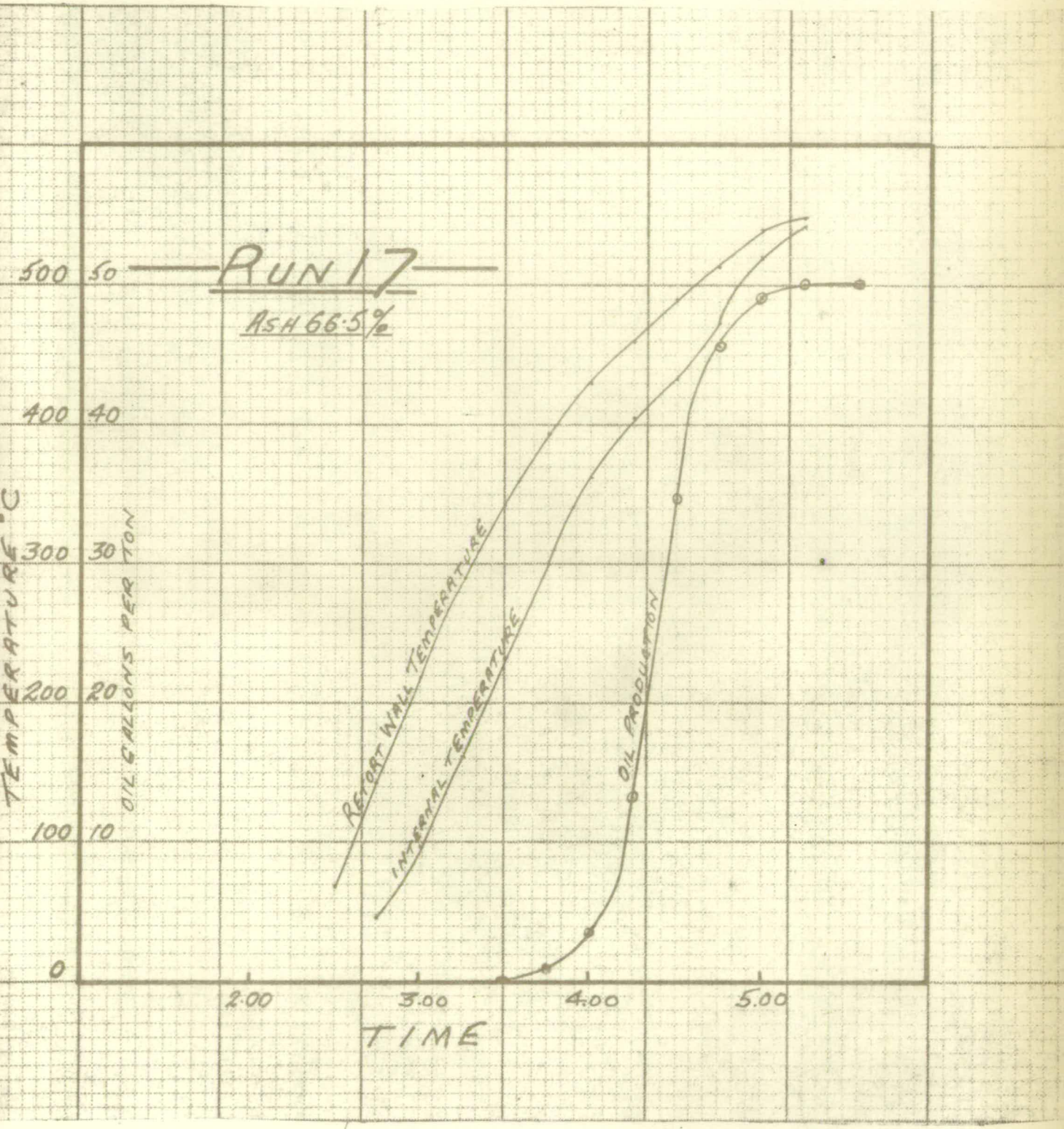
General Data

Ash/shale ratio not determined but assumed		0.665	
Kerogen percentage		33.5%	
Distillation Index		1.49	
Rate of heating in distillation range		150	deg.C/hour
Total time of oil production		1.75	hours
Maximum rate of oil production		84	galls/ton/hour
do. per % kerogen		2.50	do.
Gas production	carbon dioxide	116	cu.ft./ton
	hydrogen sulphide	~~175~~ 185	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.50	
Volatiles in residue		
Fixed carbon in residue together	7.00	20.90
Oil	20.60	61.50
Water	2.41	7.20
Carbon dioxide	0.64	1.90
Hydrogen sulphide	0.74	2.20
Other gases and loss	2.11	6.30
	100.00	100.00

Sulphur content of residue calculated to actual shale residue for comparative purposes 1.59%


RUN 17
ASH 66·5%
500
400
300
200
100
0
50
40
30
20
10
TEMPERATURE °C
OIL GALLONS PER TON
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
2.00
3.00
4.00
5.00
TIME

RUN No. 18

Charge 1120 grams standard sample, 66.5% ash, in ¼" thickness flakes mixed with 112 grams commercial 90% quicklime recently ignited to 1000 C for some hours. Room temperature 15 C.
Switched on two heats at 2.30 p.m., cut off at 5.30 p.m.
Gas scrubbed to remove hydrogen sulphide.
Scrubbed gas metered by a capillary flow meter.
Oil scrubber catches 3m.l. and 2 m.l. = 1.0 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
3.00	120	39		
3.15	214	90		
3.30	280	154		
3.45	343	221		
4.00	397	290	0.4	
4.05				5.5
4.15	440	353	3.2	10.0
4.28				21.0
4.30	473	395	14.2	
4.34				33.0
4.40				38.0
4.45	503	430	33.6	40.0
4.57				36.0
5.00	530	454	45.8	29.0
5.08				19.0
5.15	557	520	50.0	
5.17				13.0
5.30	563	546	51.0	10.0

Water condensed gallons per ton	5.4
Oil yield gallons per ton	51.0
Specific gravity of oil	0.921
Sulphur content of oil	2.26%
Saturation of oil	27%

Distillation Analysis of oil 100 m.l.

Up to 150 C	11.5%
150 to 200	10.1
200 to 250	10.1
250 to 300	12.8
Residuum by difference	55.5
	100.0

Residue

Weight 944 grams Sulphur content 2.28%

Run No. 18 continued

Sulphur distribution in products of distillation

Residue	73.8%
Oil	17.7
Hydrogen sulphide	6.4
Other gases and loss	2.1
	100.0

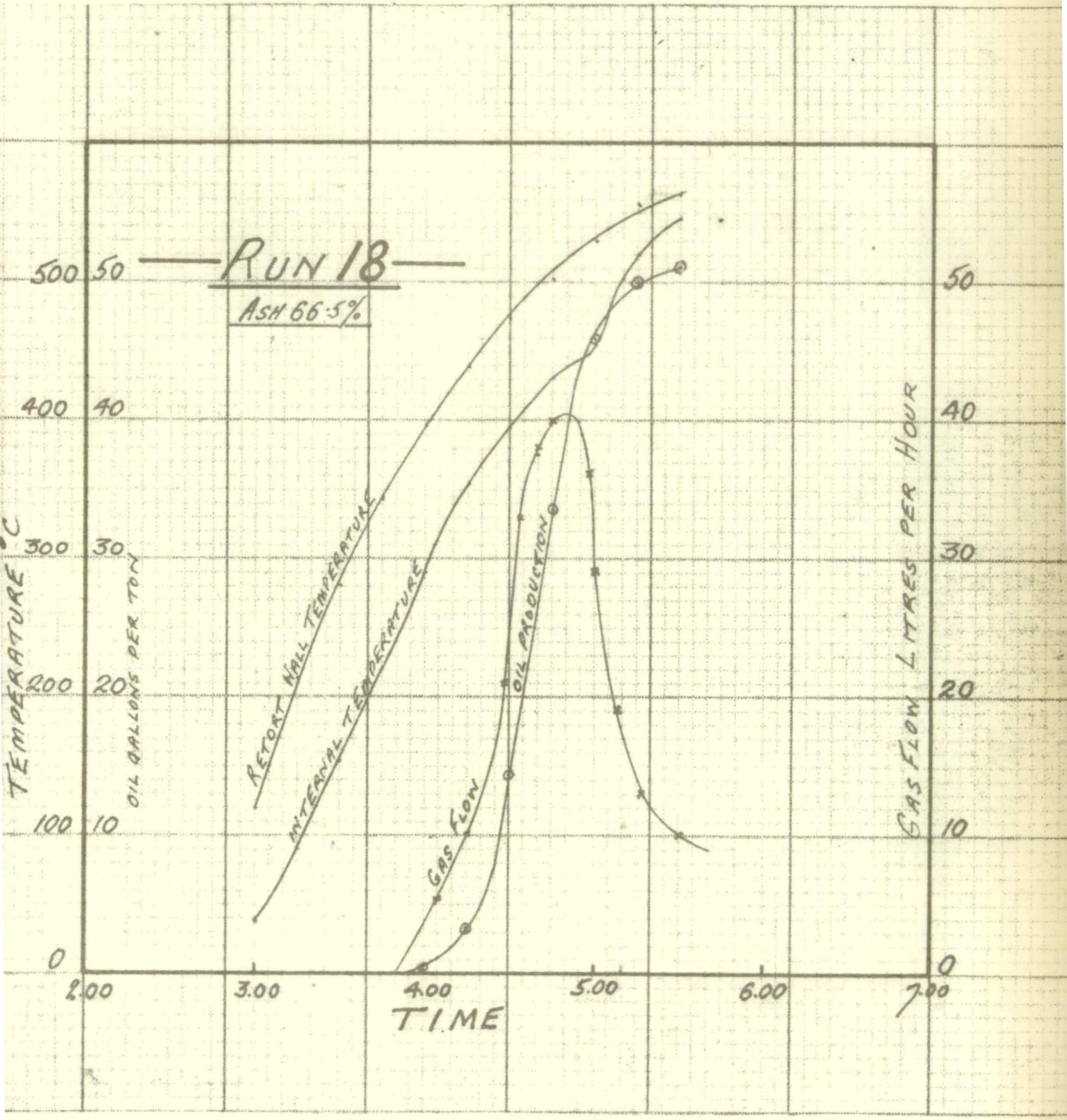
General Data

Ash/shale ratio not determined but assumed		0.665	
Kerogen percentage assumed		33.5%	
Distillation Index		1.52	
Rate of heating in distillation range		160	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		75	galls/ton/hour
do. per % kerogen		2.24	do.
Gas production	Carbon dioxide	12	cu.ft./ton
	Hydrogen sulphide	42	do.
	Scrubbed gas	977	do. N.T.P.
	Total gas	1035	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Oil	20.95	62.5%
Water	2.41	7.20

This balance is incomplete owing to the uncertain composition of the residue.


RUN 18
ASH 66·5%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00
7.00

RUN No. 19.

Charge 1120 grams standard sample, 66.6% ash, in ¼" thichness flakes. Distilled slowly.
Switched on one heat at 11.30 a.m. Cut off 9.00 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 m.l. and 2 m.l. = 1.0 gallon per ton.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
11.30	35	35		
12.00	92	37		
1.49	320	278		
2.00	335	300	0.2	
2.15	353	321	0.6	
2.30	366	341	1.0	
2.45	382	357	1.6	
3.00	396	373	2.4	3.6
3.15	408	387	4.0	5.5
3.25				7.4
3.30	420	400	7.0	
3.35				9.6
3.40				11.4
3.45	428	409	11.8	
3.50				14.8
3.57				16.0
4.00	437	418	18.2	
4.07				18.0
4.10				19.6
4.15	444	425	24.4	
4.20				18.4
4.30	451	436	30.4	18.4
4.40				17.0
4.45	457	446	34.6	15.0
5.00	466	457	37.6	
5.07				12.0
5.15	473	466	39.8	
5.22				10.0
5.30	480	473	42.0	
5.45	488	481	43.8	10.0
6.00	494	488	44.8	10.0
7.00	513	511	48.0	5.0
8.00	523	522	48.2	
9.00	532	532	48.2	

Water condensed gallons per ton	5.0
Oil yield gallons per ton	48.2
Specific gravity of oil	0.903
Sulphur content of oil	2.19%
Saturation of oil	36%

Run No. 19 continued

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	15.1%	Fractions paler than usual
150 to 200	10.7	
200 to 250	11.0	
250 to 300	12.7	
Residuum by difference	50.5	
	100.0	

Residue

Weight 833 grams Percentage of shale 74.3%

Proximate Analysis

Volatiles 4.8% Fixed carbon 5.6% Ash 89.6% Sulphur 1.69%

Sulphur distribution in products of distillation

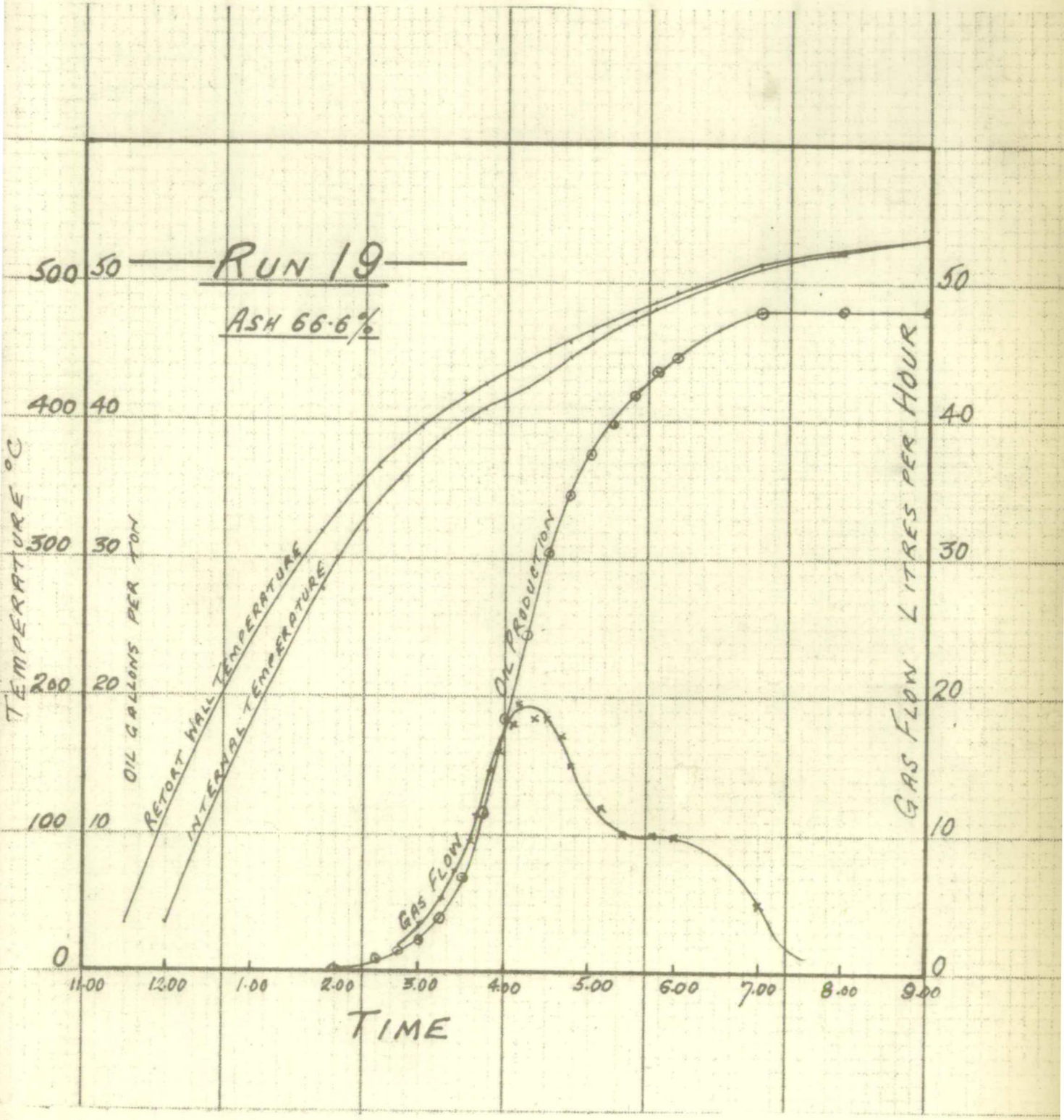
Residue	48.2%
Oil	16.8
Hydrogen sulphide	29.4
Other gases and loss	5.6
	100.0

General Data

Ash/shale ratio		0.666	
Kerogen percentage		33.4%	
Distillation index		1.44	
Rate of heating in distillation range		38	deg.C/hour
Total time of oil production		5.0	hours
Maximum rate of oil production		26	galls/ton/hour
do. per % kerogen		0.78	do.
Gas production	Carbon dioxide	63	cu.ft./ton N.T.P.
	Hydrogen sulphide	192	do.
	Scrubbed gas	1395	do.
	Total gas	1650	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.60	
Volatiles in residue	3.57	10.70%
Fixed carbon in residue	4.16	12.45
Oil	19.42	58.15
Water	2.23	6.70
Carbon dioxide	0.35	1.05
Hydrogen sulphide	0.81	2.40
Other gases and loss	2.86	8.55
	100.00	100.00


RUN 19
ASH 66·6%
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
TIME
500
400
300
200
100
0
50
40
30
20
10
0
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00

RUN No. 20

Charge 1120 grams standard sample, 66.0% ash, crushed through an 8 mesh sieve. Approximately 20% was left on a 20 mesh sieve.
Switched on one heat at 12 noon, cut off 7.10 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 m.l. and 1 m.l. = 0.8 gallon per ton.
The oil was collected in three roughly equal fractions to test out "fractional eduction" on this shale.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.00	20	16		
2.00	298	191		
2.15	317	222	0.2	
2.30	337	256	0.6	
2.47	356	282	1.0	
3.00	372	307	1.4	
3.15	387	327	2.0	
3.30	400	346	3.0	
3.35				3.6
3.45	412	364	6.0	
3.50				7.7
3.55				9.5
4.00	423	380	10.8	14.0
4.12				16.3
4.15	433	391	15.0	
4.17				23.5
4.25				20.6
4.30	442	400	24.2	
4.33				22.2
4.40				23.0
4.45	453	410	31.6	
4.55				22.8
5.00	461	420	41.8	
5.10				21.0
5.15	469	431	47.8	
5.20				16.0
5.25				14.6
5.33	474	449	50.0	
5.37				7.5
5.45	481	464	50.6	5.0
6.00	486	476	50.6	
7.10	507	501	50.6	

Water condensed gallons per ton	5.2
Oil yield gallons per ton	50.6
Sulphur content of oil computed	2.29%
Specific gravity of oil computed	0.909
Saturation of oil	28%

Run No. 20 continued

Distillation Analyses of the three fractional cuts 50 m.l.

	1st cut 74 m.l.	2nd cut 82	3rd cut 93	Calc.Avge
Up to 150 C	18.0%	13.8%	11.8%	14.4%
150 to 200	13.2	10.2	9.0	10.6
200 to 250	12.6	10.0	10.1	10.8
250 to 300	16.8	13.0	11.1	13.4
Residuum	39.4	53.0	58.0	50.8
Specific gravity	0.896	0.905	0.922	0.909
Sulphur content	3.18%	2.20%	1.68%	2.29%

Residue

Weight 825 grams Percentage of shale 73.6%

Proximate Analysis of residue

Volatiles 5.15% Fixed carbon 5.25% Ash 89.60% Sulphur 1.93%

Sulphur distribution in products of distillation

Residue	54.7%
Oil	18.0
Hydrogen sulphide	22.8
Other gases and loss	4.5
	100.0

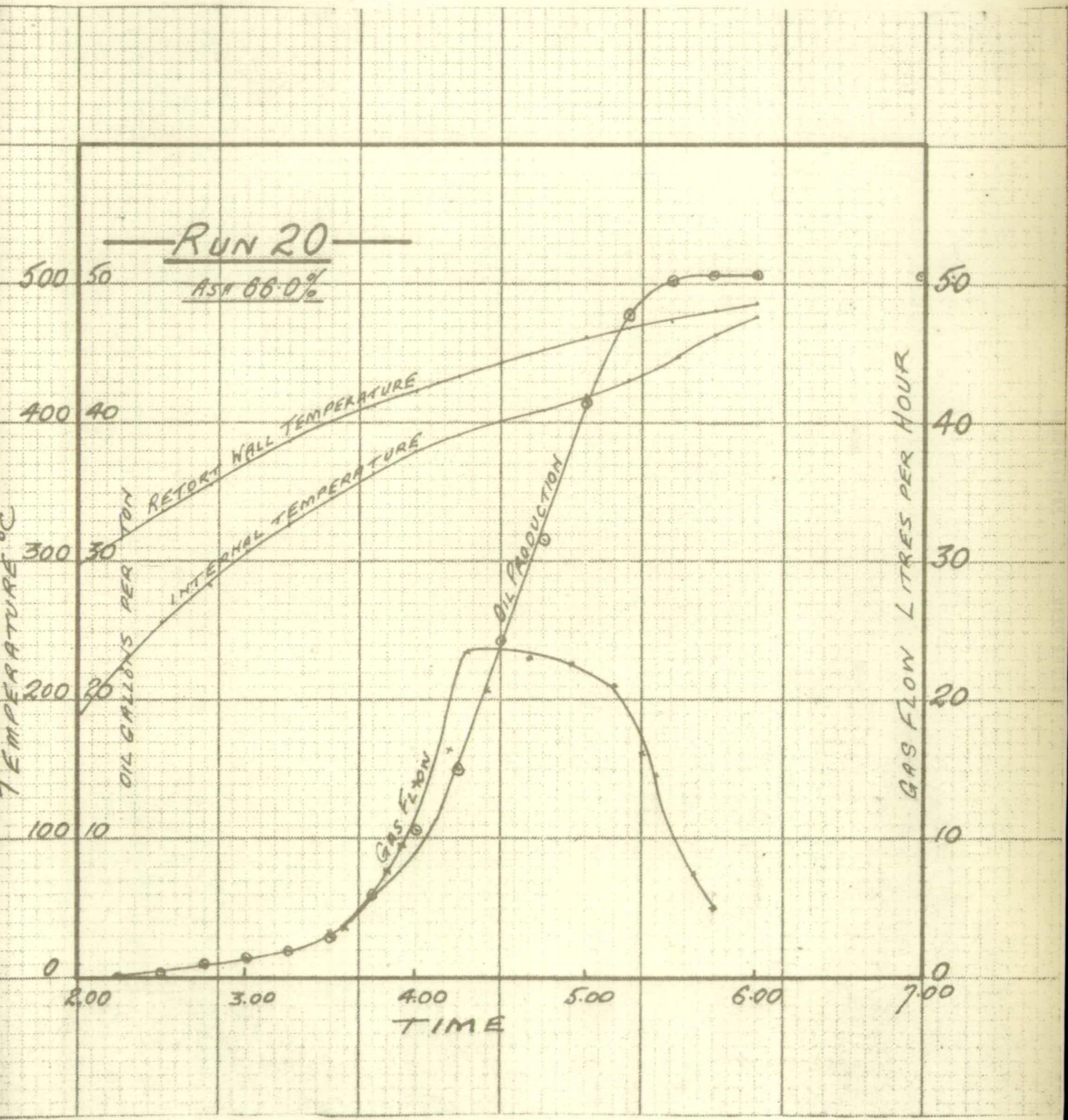
General Data

Ash/shale ratio		0.660	
Kerogen percentage		34.0%	
Distillation Index		1.49	
Rate of heating in distillation range		45	deg.C/hour
Total time of oil production		3.5	hours
Maximum rate of oil production		34	galls/ton/hour
do. per % kerogen		1.00	do.
Gas production	Carbon dioxide	108	cu.ft./ton N.T.P.
	Hydrogen sulphide	149	do.
	Scrubbed gas	1202	do.
	Total gas	1459	do.

Run No. 20 continued

Weight Distribution of the products of distillation

	Percent of shale	On ashless basis
Ash	66.0	
Volatiles in residue	3.78	10.90%
Fixed carbon in residue	3.86	11.35
Oil	20.55	60.60
Water	2.32	6.85
Carbon dioxide	0.60	1.80
Hydrogen sulphide	0.63	1.85
Other gases and loss	2.26	6.65
	100.00	100.00


RUN 20
ASH 66·0%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
TEMPERATURE °C
OIL GALLONS PER HOUR
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00
7.00

RUN No. 21

Charge 1120 grams standard sample, 66.5% ash, and crushed through a 20 mesh sieve.
Switched on two heats at 2.35 p.m., cut back to one heat at 5.45.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 4 m.l. and 2 m.l. = 1.2 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.35	18	18		
2.45	35	18		
3.00	95	26		
3.17	180	60		
3.30	248	101		
3.45	310	126		
4.00	359	175	0.2	
4.15	403	233	1.2	4.0
4.28				7.5
4.30	439	287	2.6	15.0
4.34				19.5
4.36				24.0
4.41				31.3
4.43				33.5
4.45	471	342	13.4	
4.48				33.5
4.53				36.5
4.58				37.4
5.00	499	382	30.4	38.2
5.07				38.7
5.13				38.2
5.15	523	410	43.8	
5.20				35.0
5.25				30.5
5.30	546	443	50.6	
5.32				23.0
5.36				15.0
5.40				10.8
5.45	568	505	51.4	9.0
5.52				6.5
6.00			51.4	4.0

Water condensed gallons per ton	5.0
Oil yield gallons per ton	51.4
Specific gravity of oil	0.925
Sulphur content of oil	2.37%
Saturation of oil	18%

Run No. 21 continued

Distillation Analysis of crude oil 100 m.l.

UP to 150 C	13.1%
150 to 200	9.2
200 to 250	11.3
250 to 300	10.9
Residuum	55.5
	100.0

Residue

Weight 813 grams Percentage of shale 72.6%

Proximate Analysis of residue

Volatiles 3.85% Fixed carbon 4.60% Ash 91.55% Sulphur 2.01%

Sulphur distribution in products of distillation

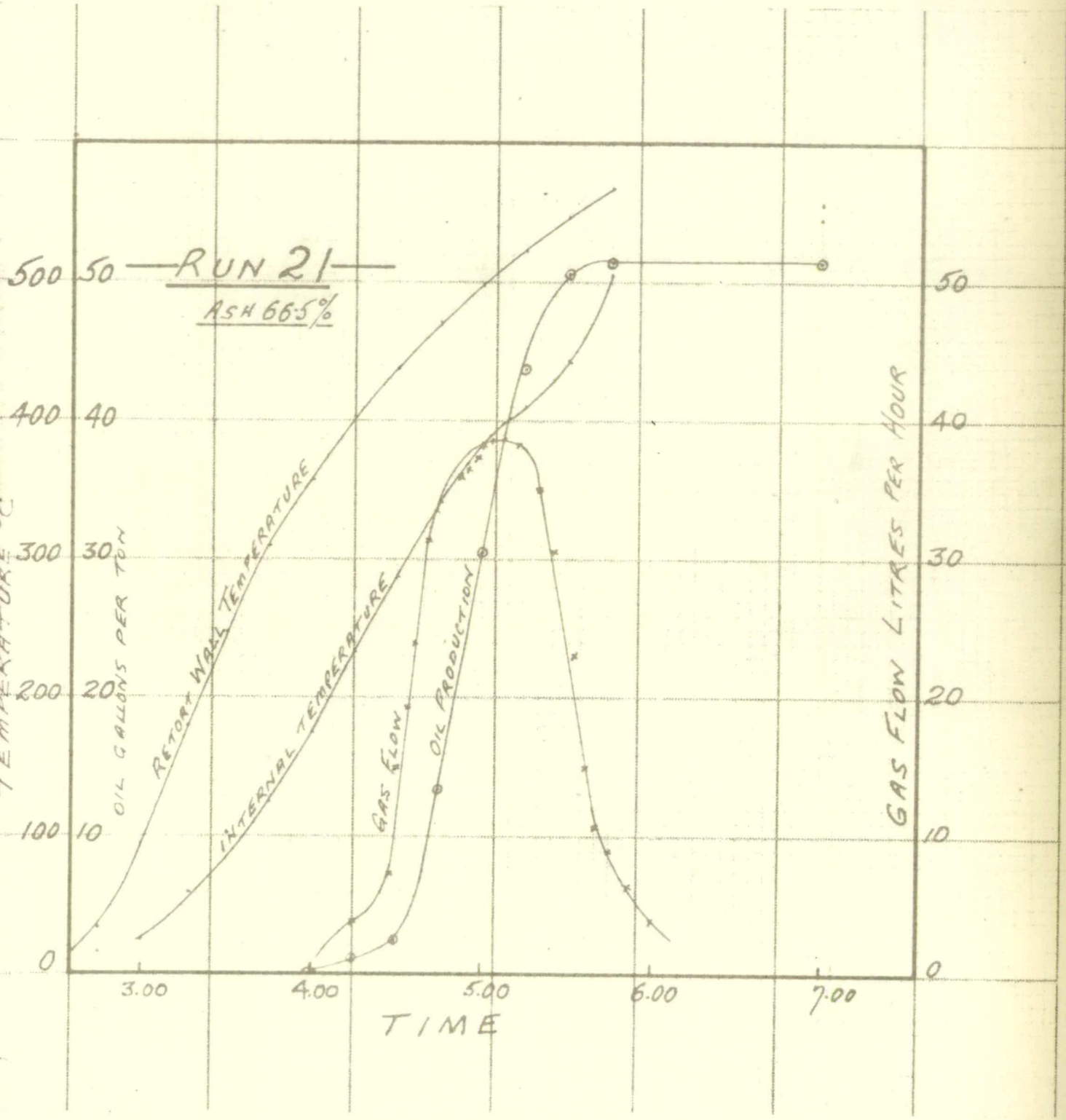
Residue	56.1%	The reason for this over-recovery could not be found. The assays were checked again without material change. Possibly more pyrite was present than usual.
Oil	17.2	
Hydrogen sulphide	30.5	
Over-recovery	3.8	

General Data

Ash/shale ratio		0.665	
Kerogen percentage		33.5%	
Distillation Index		1.53	
Rate of heating in distillation range		140	deg.C/hour
Total time of oil production		1.75	hours
Maximum rate of oil production		65	galls/ton/hour
do. per % kerogen		1.94	do.
Gas production	Carbon dioxide	73	cu.ft./ton N.T.P.
	Hydrogen sulphide	197	do.
	Scrubbed gas	1248	do.
	Total gas	1518	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.50	
Volatiles in residue	2.80	8.35%
Fixed carbon in residue	3.34	9.95
Oil	21.0	62.70
Water	2.23	6.65
Carbon dioxide	0.40	1.20
Hydrogen sulphide	0.83	2.50
Other gases and loss	2.90	8.65
	100.00	100.00


RUN 21
ASH 66·5%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TEMPERATURE °C
500
400
300
200
100
0
50
40
30
20
10
0
3.00
4.00
5.00
6.00
7.00
TIME

RUN No. 22

Charge 1120 grams standard sample, 66.8% ash, in pieces of ½" minimum size. Room temperature 13 C.
Switched on two heats at 6.45 p.m., cut off at 9.45 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 4 m.l. and 2 m.l. = 1.2 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
7.00	53	20		
7.15	105	44		
7.30	227	97		
7.45	300	161		
8.02	362	249	0.1	
8.15	407	320	1.0	5.0
8.20				5.5
8.25				9.5
8.30	450	384	3.6	20.5
8.35				30.5
8.40				40.0
8.45	483	430	23.4	45.0
8.50				46.5
8.55				44.0
9.00	514	471	44.0	36.6
9.05				30.0
9.10				23.5
9.15	543	522	48.4	18.0
9.20				14.5
9.25				12.5
9.30	570	552	50.0	10.0
9.35				9.0
9.40				8.0
9.45	589	578	50.2	6.8

Water condensed gallons per ton	6.0
Oil yield gallons per ton	50.4
Specific gravity of oil	0.922
Sulphur content of oil	2.52%
Saturation of oil	21%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	11.8%
150 to 200	10.1
200 to 250	11.0
250 to 300	11.5
Residuum	55.6
	100.0

Run No. 22 continued

Residue

Weight 820 grams Percent of shale 73.1%

Proximate Analysis of residue

Volatiles 4.2% Fixed carbon 4.45% Ash 91.35% Sulphur 1.76%

Sulphur distribution in products of distillation

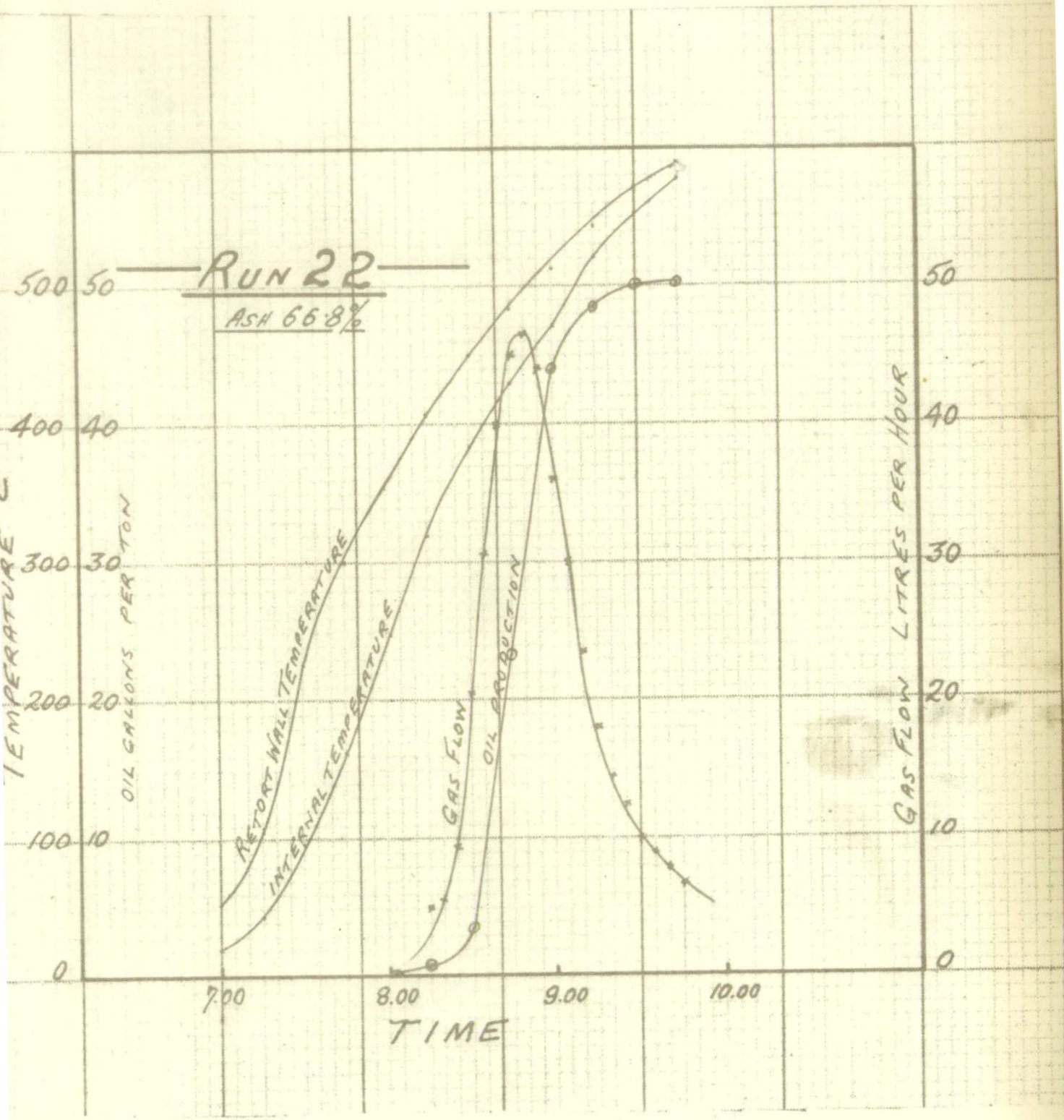
Residue	49.5%
Oil	20.1
Hydrogen sulphide	27.4
Other gases and loss	3.0
	100.0

General Data

Ash/shale ratio		0.668	
Kerogen percentage		33.2	
Distillation Index		1.52	
Rate of heating in distillation range		175	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		80	galls/ton/hour
do. per % kerogen		2.41	do.
Gas production	Carbon dioxide	62	cu.ft./ton N.T.P.
	Hydrogen sulphide	179	do.
	Scrubbed gas	1008	do.
	Total gas	1249	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.80	
Volatiles in residue	3.08	9.30%
Fixed carbon in residue	3.26	9.75
Oil	20.70	62.40
Water	2.68	8.05
Carbon dioxide	0.34	1.05
Hydrogen sulphide	0.75	2.25
Other gases and loss	2.39	7.20
	100.00	100.00


RUN 22
ASH 66·8%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
7.00
8.00
9.00
10.00

RUN No. 23

Charge 1120 grams standard sample, 65.6% ash, in flakes ¼" maximum thickness.
Distilled moderately fast to check Run 15 and intervening work.
Switched on two heats at 12.45 p.m.
Room temperature 16 C, barometer 761 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 4.5 m.l. and 2 m.l. = 1.3 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	GAS PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.04	374		0.2	
2.15	415	292	1.6	4.0
2.20				8.0
2.25				15.4
2.30	455	372	5.4	23.5
2.35				31.0
2.40				40.0
2.45	486	412	25.4	43.5
2.50				44.0
2.55				43.0
3.00	517	448	46.2	40.0
3.05				31.0
3.10				25.0
3.15	546	507	52.6	18.0
3.20				13.5
3.25				9.5
3.30	570	544	52.6	7.0

Water condensed gallons per ton	5.0
Oil yield gallons per ton	52.6
Specific gravity of oil	0.922
Sulphur content of oil	2.52%
Saturation of oil	27%

Distillation Analysis of oil 100 m.l.

Up to 150 C	11.0%
150 to 200	9.6
200 to 250	10.8
250 to 300	11.0
Residuum by difference	57.6
	100.0

Residue

Weight 807 grams Percent of shale 72.0%

Run No. 23 continued

Proximate analysis of residue

Volatiles 4.65% Fixed carbon 4.25% Ash 91.1% Sulphur 1.61%

Sulphur distribution in products of distillation

Residue	44.6%
Oil	20.3
Hydrogen sulphide	30.9
Other gases and loss	4.2
	100.0

General Data

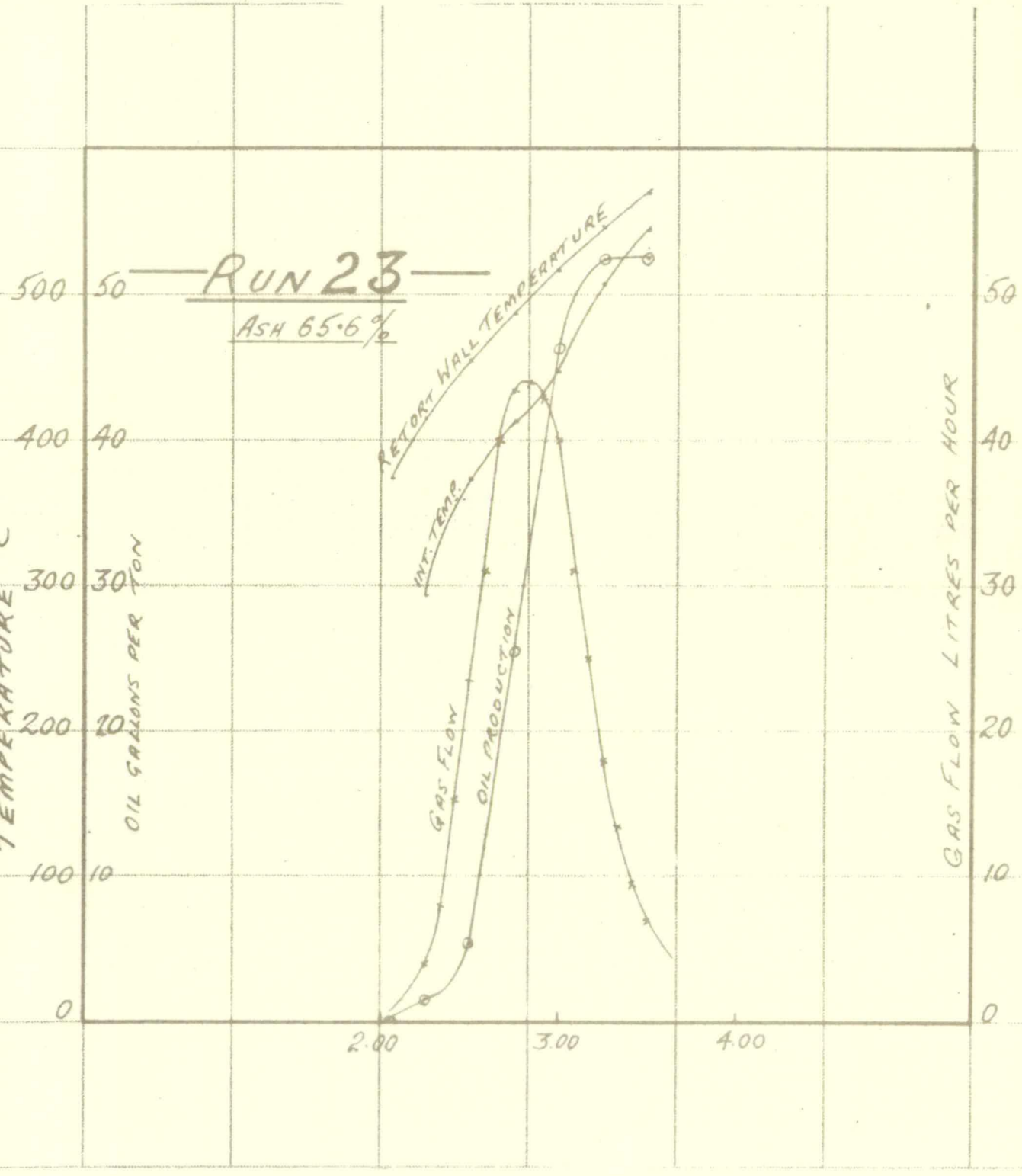
Ash/shale ratio		0.656	
Kerogen percentage		34.4	
Distillation Index		1.52	
Rate of heating in distillation range		165	deg.C/hour
Total time of oil production		1.25	hours
Maximum rate of oil production		82	galls/ton/hour
do. per % kerogen		2.38	do.
Gas production	Carbon dioxide	55	cu.ft./ton N.T.P.
	Hydrogen sulphide	202	do.
	Scrubbed gas	1018	do.
	Total gas	1275	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	65.6	
Volatiles in residue	3.35	9.75%
Fixed carbon in residue	3.06	8.90
Oil	21.50	62.50
Water	2.23	6.50
Carbon dioxide	0.30	0.85
Hydrogen sulphide	0.85	2.45
Other gases and loss	3.11	9.05
	100.00	100.00

General Note

This run is not as representative as Run 15 as a small gasket leak occurred. The leak was small only as reflected in the moderate increase in the loss item in the weight balance. It was sufficient, however, to offset the increased richness of shale and to reduce the oil yield to that of Run 15. It demonstrates also that the Distillation Index is a closer expression of efficiency of distillation.


RUN 23
ASH 65·6 %
RETORT WALL TEMPERATURE
INT. TEMP.
GAS FLOW
OIL PRODUCTION
TEMPERATURE C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00

RUN No. 24

Charge 1120 grams standard sample, 65.7% ash, crushed to flakes not exceeding 3/16" thickness.
Distilled at a very fast rate.
Switched on two heats at 9.40 a.m. Cut off 11.30 a.m.
Room temperature 21 C . Barometer 761 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 6m.l. and 2.5 m.l. = 1.7 gallons per ton.

TIME A.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
10.00	130	25		
10.30	352	147		
10.35				3.6
10.45	433	250	1.0	5.0
10.50				12.0
10.55				21.3
11.00	487	345	9.8	35.5
11.05				45.0
11.10				50.0
11.15	534	410	35.8	53.5
11.20				58.0
11.25				55.0
11.30	575	471	50.0	44.0
11.35	580			19.3
11.40				10.0
11.45	563	546	51.0	4.0
11.50				2.0

Water condensed gallons per ton	6.0
Oil yield gallons per ton	51.0
Specific gravity of oil	0.927
Sulphur content of oil	2.59%
Saturation of oil	27%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	13.0%
150 to 200	10.5
200 to 250	9.2
250 to 300	13.8
Residuum	53.5
	100.0

Residue

Weight 807 grams Percentage of shale 72.0%

Run No. 24 continued

Proximate Analysis of residue

Volatiles 4.7% Fixed carbon 4.15% Ash 91.15% Sulphur 1.86%

Sulphur distribution in products of distillation

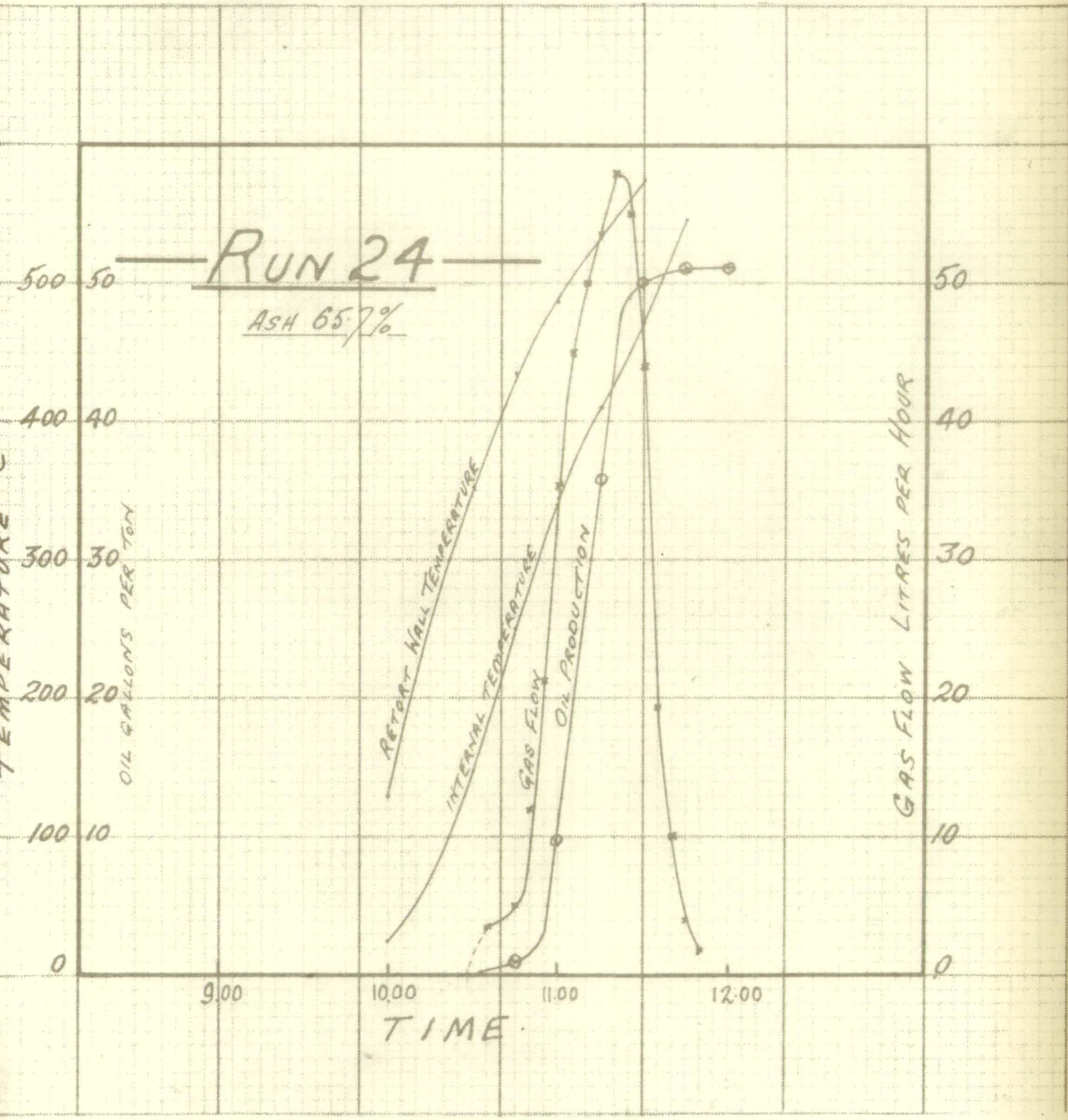
Residue	51.5%
Oil	20.3
Hydrogen sulphide	28.0
Other gases and loss	0.2
	100.0

General Data

Ash/shale ratio		0.656	
Kerogen percentage		34.4	
Distillation Index		1.48	
Rate of heating in distillation range		260	deg.C/hour
Total time of oil production		1.0	hours
Maximum rate of oil production		103	galls/ton/hour
do. per % kerogen		3.0	do.
Gas production	Carbon dioxide	113	cu.ft./ton N.T.P.
	Hydrogen sulphide	183	do.
	Scrubbed gas	1057	do.
	Total gas	1353	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	65.6	
Volatiles in residue	3.38	9.80%
Fixed carbon in resdiue	2.99	8.70
Oil	21.10	61.35
Water	2.68	7.80
Carbon dioxide	0.62	1.80
Hydrogen sulphide	0.77	2.25
Other gases and loss	2.86	8.30
	100.00	100.00


RUN 24
ASH 65.7%
500
400
300
200
100
0
50
40
30
20
10
0
TEMPERATURE
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
9.00
10.00
11.00
12.00
TIME

RUN No. 25

Charge 1120 grams standard sample, 66.5% ash, in the largest pieces which would go in the retort, minimum dimensions ¾" to 1".
Distilled at very fast rate.
Switched on two heats at 6.30 p.m., cut back to one heat at 8.15.
Room temperature 14 C. Barometer 759 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches, 5 m.l. and 3 m.l. = 1.6 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
7.00	206	84		
7.15	316	176		
7.30	394	283	0.2	2.0
7.40				8.0
7.45	463	392	3.0	18.0
7.50				34.0
7.55				52.0
8.00	514	457	30.8	57.0
8.05				58.0
8.10				52.0
8.15	560	520	49.0	43.0
8.20	571	538	49.8	36.0
8.25	571	550	50.6	24.0
8.30	568	554	50.8	13.5
8.35				8.5
8.40				5.0
8.45	559	554	51.0	3.0
9.00	550	546	51.0	

Water condensed gallons per ton	5.0
Oil yield gallons per ton	51.0
Specific gravity of oil	0.924
Sulphur content of oil	2.43%
Saturation of oil	21%

Distillation Analysis of crude oil 100 m.l.

Up to 150 C	12.3%
150 to 200	10.3
200 to 250	10.6
250 to 300	12.0
Residuum	54.8
	100.0

Residue

Weight 817 grams Percentage of shale 73.0%

Run No. 25 continued

Proximate analysis of residue

Volatiles 4.95% Fixed carbon 3.90% Ash 91.15% Sulphur 1.67%

Sulphur distribution in products of distillation.

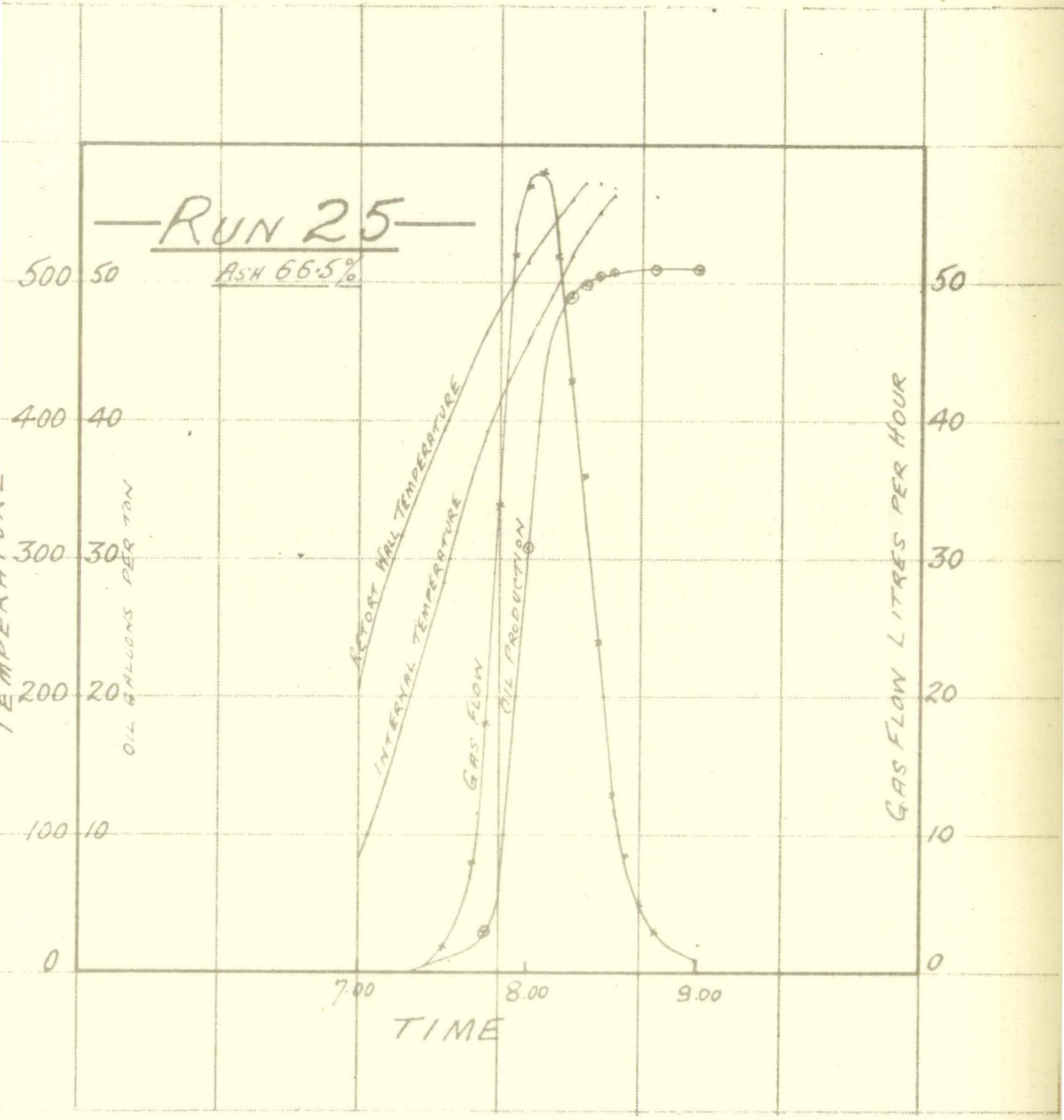
Residue	46.8%
Oil	19.1
Hydrogen sulphide	27.4
Other gases and loss	6.7
	100.0

General Data

Ash/shale ratio		0.665	
Kerogen percentage		33.5	
Distillation Index		1.52	
Rate of heating in distillation range		280	deg.C/hour
Total time of oil production		1.0	hours
Maximum rate of oil production		144	galls/ton/hour
do. per % kerogen		4.30	do.
Gas production	Carbon dioxide	77	cu.ft./ton N.T.P.
	Hydrogen sulphide	179	do.
	Scrubbed gas	1057	do.
	Total gas	1313	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.5%	
Volatiles in residue	3.62	10.80%
Fixed carbon in residue	2.94	8.80
Oil	21.00	62.70
Water	2.23	6.65
Carbon dioxide	0.42	1.25
Hydrogen sulphide	0.76	2.25
Other gases and loss	2.53	7.55
	100.00	100.00


RUN 25
ASH 66·5%
500
400
300
200
100
0
50
40
30
20
10
0
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
7.00
8.00
9.00
TIME

RUN No. 26

Charge 1120 grams standard sample, 67.2% ash, crushed to 3/16" thickness flakes.
Distilled at a very slow rate.
Switched on one heat at 9.00 a.m.
Room temperature 20 C average. Barometer varied 751 to 748 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 m.l. and 2 m.l. = 1.0 gallon per ton.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
10.30	223	147		
11.00	270	209		
11.30	310	270		
12.00	344	310	0.2	1.4
12.30	367	349	1.0	2.0
1.00	382	372	2.4	4.5
1.15	389	380	3.8	5.4
1.30	394	386	5.6	7.0
1.45	399	392	8.0	7.5
2.00	402	396	10.0	8.5
2.15	404	398	12.6	8.5
2.30	406	400	14.8	8.5
2.45	407	401	17.0	8.2
3.00	409	403	19.2	8.2
3.15	410	405	21.0	7.5
3.30	411	406	22.2	6.7
3.45	412	409	23.8	6.0
4.00	413	411	24.8	6.4
4.15	415	414	26.2	6.7
4.30	418	417	27.6	6.7
4.45	421	421	29.0	6.7
5.00	425	425	30.4	6.0
5.15	429	429	31.4	5.4
5.30	431	431	32.0	4.7
5.45	432	432	32.6	4.2
6.00	433	433	32.8	3.5
6.15		435	33.2	2.8
6.30		437	33.6	2.8
6.45		439	33.8	2.8
7.00		441	34.4	2.8
7.15		444	35.0	2.8
7.30		447	35.4	2.8
7.45		449	35.8	2.8
8.00		450	36.4	2.5
8.15		453	36.6	2.5
8.30		455	37.0	2.5
8.45		459	37.4	2.5

Run No. 26 continued

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
9.00		463	37.8	2.5
9.15		468	38.4	3.0
9.30		473	39.0	3.5
9.45		478	39.6	3.5
10.00		481	39.8	3.0
10.15		484	40.2	3.0
Next day				
10.00		494	41.6	

Remarks

Removed radiation shield from furnace at 12.00 noon to reduce rate of rise of temperature. At 1.30 p.m. removed end plugs of furnace for same purpose. Replaced end plugs at 3.45 p.m. At 6.00 p.m. the wall temperature thermocouple burnt through. It is suspected that the wall temperatures for one or two hours previous to burning out are one or two degrees too low. This would explain the absence of a temperature difference between the two couples.
At 6.15 the furnace ends were lagged to raise the rate of rise of temperature and at 8.00 p.m. the furnace shield was replaced for the same purpose.
Oil was slowly coming over at 10.15 p.m. so furnace was left on overnight and power cut off at 10.00 a.m. next day.

Water condensed gallons per ton	5.2
Oil yield gallons per ton	41.6
Specific gravity of oil	0.897
Sulphur content of oil	2.29%
Saturation of oil	39%

Distillation analysis of crude oil 100 m.l.

Up to 150 C	14.7%
150 to 200	13.9
200 to 250	11.7
250 to 300	15.6
Residuum	44.1
	100.0

Residue

Weight 859 grams Percentage of shale 76.6%

Run No. 26 continued

Proximate analysis of residue

Volatiles 5.45% Fixed carbon 6.75% Ash 87.8% Sulphur 1.83%

Sulphur distribution in products of distillation

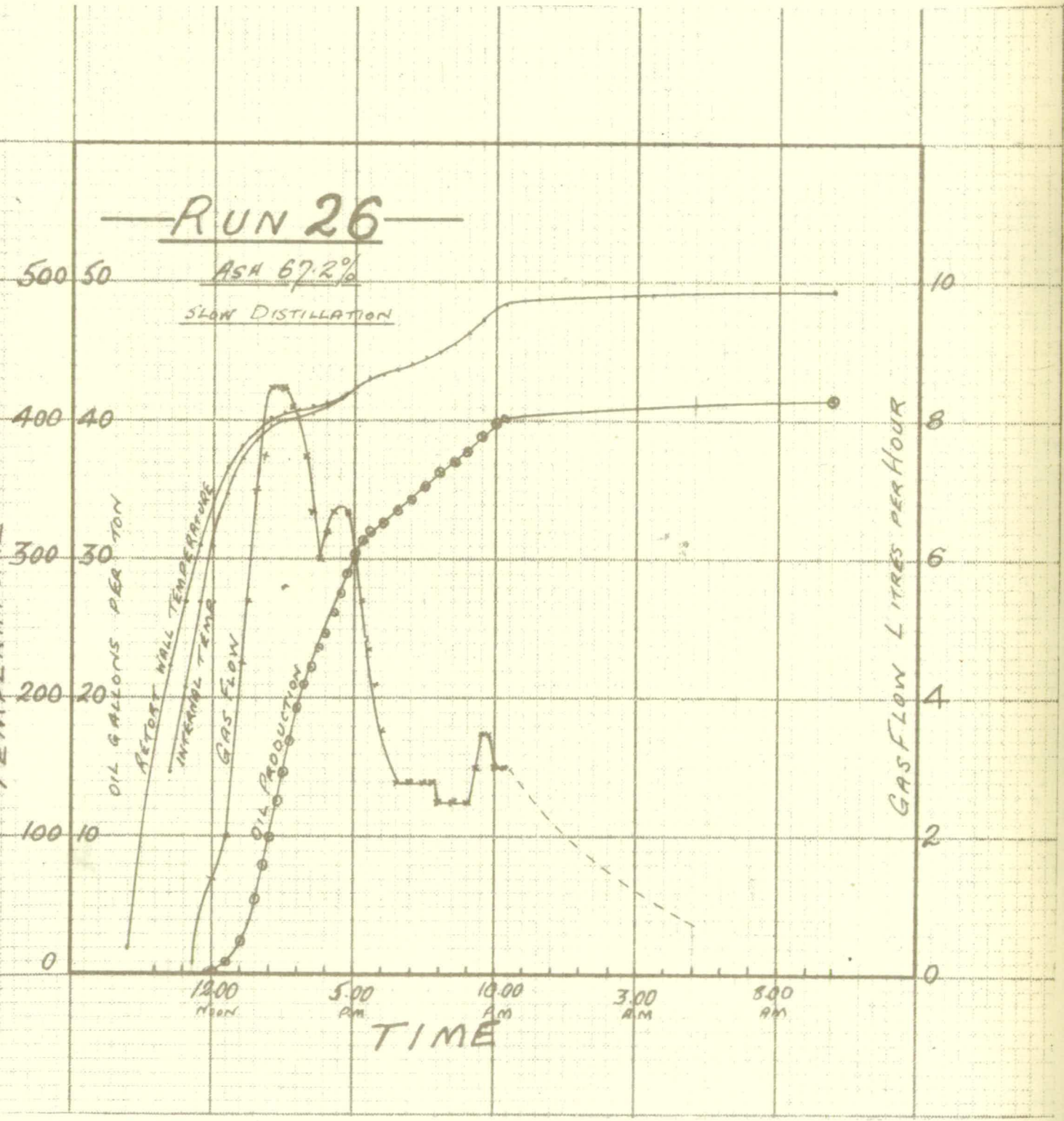
Residue	53.9%
Oil	14.4
Hydrogen sulphide	27.1
Other gases and loss	4.6
	100.0

General Data

Ash/shale ratio		0.672	
Kerogen percentage		32.8	
Distillation Index		1.27	
Rate of heating in distillation range		10	deg.C/hour
Total time of oil production		12	hours
Maximum rate of oil production		10	galls/ton/hour
do. per % kerogen		0.30	do.
Gas production	Carbon dioxide	65	cu.ft./ton N.T.P.
	Hydrogen sulphide	177	do.
	Scrubbed gas	1847	do.
	Total gas	2089	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	67.2	
Volatiles in residue	4.18	12.75%
Fixed carbon in residue	5.18	15.70
Oil	16.68	50.90
Water	2.32	7.10
Carbon dioxide	0.36	1.10
Hydrogen sulphide	0.75	2.30
Other gases and loss	3.33	10.15
	100.00	100.00


RUN 26
ASH 67.2%
SLOW DISTILLATION
500
400
300
200
100
0
50
40
30
20
10
0
10
8
6
4
2
0
OIL GALLONS PER TON
RETORT WALL TEMPERATURE
INTERNAL TEMP
GAS FLOW
OIL PRODUCTION
GAS FLOW LITRES PER HOUR
12.00 NOON
5.00 PM
10.00 PM
3.00 AM
8.00 AM
TIME

RUN No. 27

Charge 1120 grams standard sample, 66.5% ash, crushed through a 20 mesh screen.
Distilled as fast as furnace would allow.
Switched on two heats at 3.15 p.m., cut back to one heat at 5.11.
Room temperature 17 C. Barometer 761 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 6 m.l. and 4 m.l. = 2.0 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
3.30	72	21		
4.00	280	94		
4.15	377	119		3.5
4.30	448	185	1.0	7.0
4.35				14.5
4.40			6.2	26.0
4.45	495	275	9.6	32.5
4.50			15.0	38.5
4.55			20.4	42.1
5.00	538	352	27.0	45.0
5.05	546	372	31.8	48.5
5.11	563	390	37.4	50.4
5.15	571	400	40.0	51.4
5.20	571	418	43.0	46.0
5.26	564	436	45.6	35.5
5.30	563	449	46.8	26.0
5.35	559	469	47.2	13.0
5.40	556	494	47.2	6.0
5.50	549	519	47.2	2.5

Water condensed gallons per ton	7.0
Oil yield gallons per ton	47.2
Specific gravity of oil	0.928
Sulphur content of oil	2.32%
Saturation of oil	22%

Distillation Analysis of oil 100 m.l.

Up to 150 C	13.2%
150 to 200	11.0
200 to 250	10.7
250 to 300	12.8
Residuum	52.3
	100.0

Residue

Weight 820 grams Percentage of shale 73.2%

Run No. 27 continued

Proximate analysis of residue

Volatiles 4.60% Fixed carbon 4.70% Ash 90.7% Sulphur 2.09%

Sulphur distribution in products of distillation

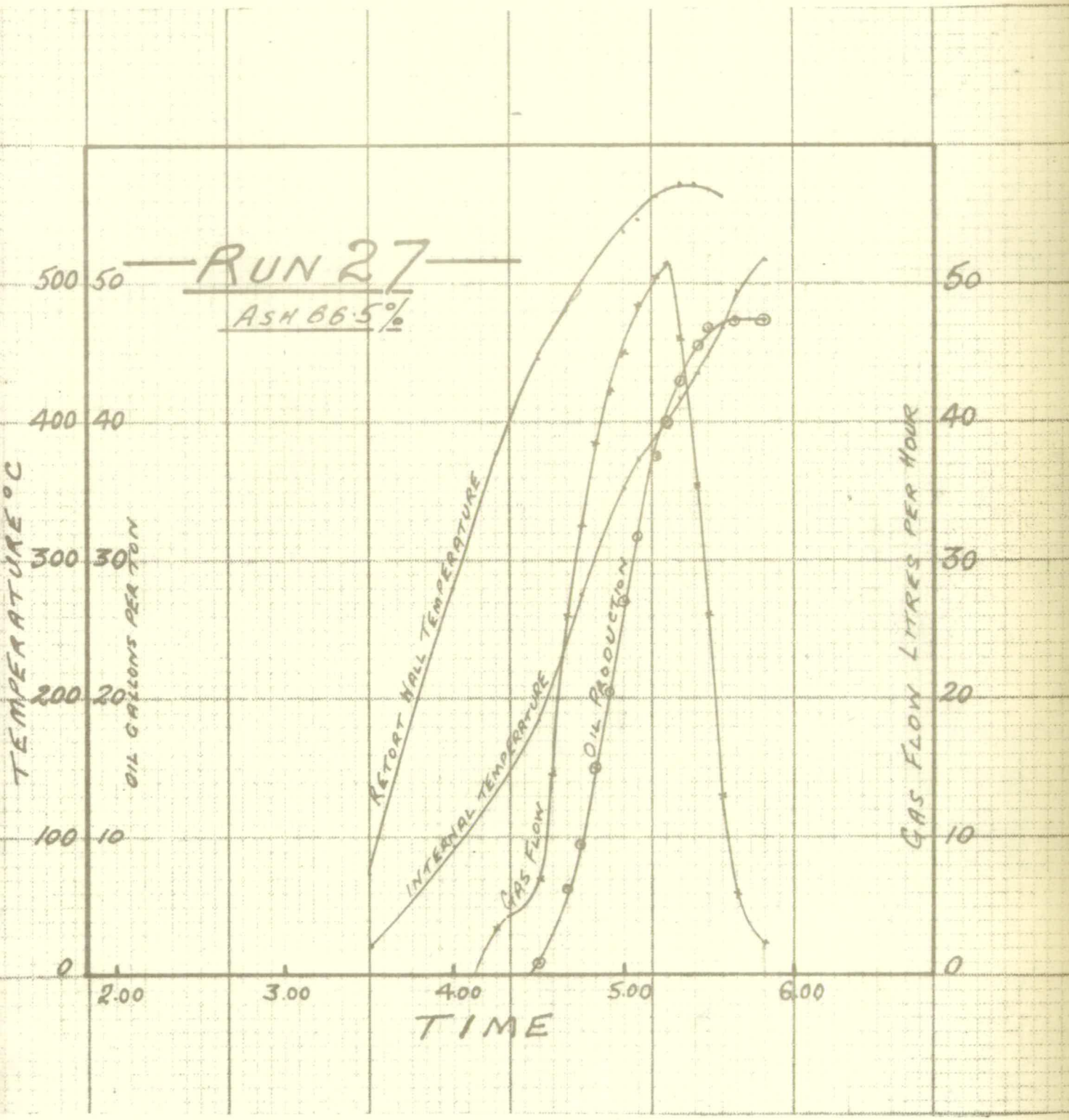
Residue	58.9%
Oil	16.7
Hydrogen sulphide	20.8
Other gases and loss	3.6
	100.0

General Data

Ash/shale ratio		0.665	
Kerogen percentage		33.5%	
Distillation Index		1.41	
Rate of heating in distillation range		200	deg.C/hour
Total time of oil production		1.25	hours (bare)
Maximum rate of oil production		70	gallons/ton/hour
do. per % kerogen		2.09	do.
Gas production	Carbon dioxide	77	cu.ft./ton N.T.P.
	Hydrogen sulphide	136	do.
	Scrubbed gas	1302	do.
	Total gas	1515	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.45%	
Volatiles in residue	3.36	10.00%
Fixed carbon in residue	3.44	10.25
Oil	19.55	58.30
Water	3.12	9.30
Carbon dioxide	0.42	1.25
Hydrogen sulphide	0.57	1.70
Other gases and loss	3.09	9.20
	100.00	100.00


RUN 27
ASH 66·5%
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 28

Charge 1120 grams standard sample, 66.8% ash, in flakes 3/16"to ¼" thickness.
Retorted at fastest possible rate.
Switched on 2 heats at 10.20 a.m., cut back to one heat at 12.10 cut off 12.30 p.m.
Room temperature 21 C. Barometer 756 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 6 m.l. and 4 m.l. = 2.0 gallons per ton.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
10.45	125	30		
11.00	260	88		
11.15	357	147		1.5
11.20	388	175		2.2
11.25	410	210		3.5
11.30	434	249	0.6	7.5
11.35	457	283	1.4	12.5
11.40	474	320	6.0	31.0
11.45	490	352	8.4	42.0
11.50	507	378	17.4	50.3
11.55	524	400	26.4	64.5
12.00	541	425	37.6	69.5
12.05	557	442	43.4	71.1
12.10	572	466	47.4	61.5
12.15	585	507	48.2	29.5
12.20	585	529	48.8	14.0
12.25	583	544	48.8	9.0

Water condensed gallons per ton	6.0
Oil yield galloms per ton	48.8
Specific gravity of oil	0.927
Sulphur content of oil	2.37%
Saturation of oil	22%

Distillation analysis of oil 100 m.l.

Up to 150 C	11.9%
150 to 200	11.0
200 to 250	10.5
250 to 300	12.4
Residuum	54.2
	100.0

Residue

Weight 817 grams Percentage of shale 73.0%

Run No. 28 continued

Proximate analysis of residue

Volatiles 4.2% Fixed carbon 4.1% Ash 91.7% Sulphur 1.90%

Sulphur distribution in products of distillation

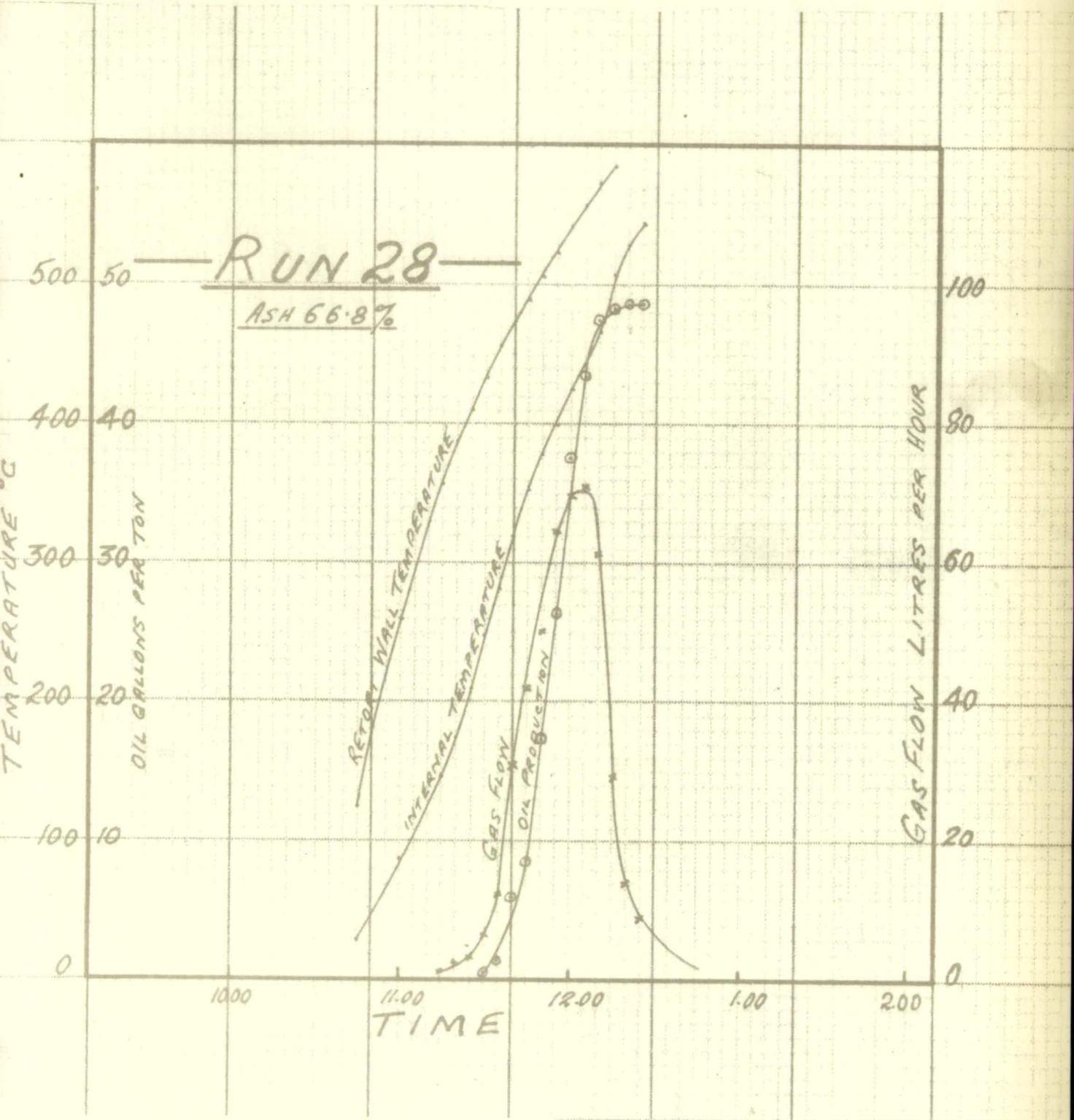
Residue	53.2%
Oil	17.6
Hydrogen sulphide	25.2
Other gases and loss	4.0
	100.0

General Data

Ash/shale ratio		0.668	
Kerogen percentage		33.2%	
Distillation Index		1.47	
Rate of heating in distillation range		280	deg.C/hour
Total time of oil production		0.75	hour
Maximum rate of oil production		109	galls/ton/hour
do. per % kerogen		3.28	do.
Gas production	Carbon dioxide	75	cu.ft./ton N.T.P.
	Hydrogen sulphide	164	do.
	Scrubbed gas	1190	do.
	Total gas	1429	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.85	
Volatiles in residue	3.06	9.20%
Fixed carbon in residue	2.99	9.00
Oil	20.20	60.95
Water	2.68	8.10
Carbon dioxide	0.41	1.25
Hydrogen sulphide	0.70	2.10
Other gases and loss	3.11	9.40
	100.00	100.00


RUN 28
ASH 66·8%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
100
80
60
40
20
0
10.00
11.00
12.00
1.00
2.00

RUN No. 29

Charge 1120 grams standard sample, 65.7% ash, in pieces of ¼" minimum dimension.
Distilled at very fast rate.
Switched on two heats at 3.00 p.m., cut off 5.00 p.m.
Room temperature 18 C. Barometer 753 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 6.5 and 3.5 m.l. = 2.0 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
3.30	205	73		
3.45	320	161		
4.00	410	280		3.5
4.05	432	314	0.6	6.0
4.10	457	356	2.0	14.0
4.15	476	385	3.6	31.0
4.20	492	410	11.8	48.5
4.25	511	431	25.6	71.0
4.30	527	452	37.8	77.0
4.35	536	475	47.6	67.0
4.40	542?	500	51.0	42.0
4.45	544	516	52.4	26.0
4.50	550	530	52.6	15.0
4.55	554	538	52.6	9.2
5.00	554	542	52.6	5.5
5.15		546	52.6	

Water condensed gallons per ton	5.0
Oil yield gallons per ton	52.6
Specific gravity of oil	0.926
Sulphur content of oil	2.41%
Saturation of oil	26%

Distillation analysis of crude oil

Up to 150 C	11.1%
150 to 200	10.6
200 to 250	9.8
250 to 300	11.9
Residuum	56.6
	100.0

Residue

Weight 807.5 grams Percentage of shale 72.0%

Run No. 29 continued

Proximate analysis of residue

Volatiles 4.75% Fixed carbon 4.20% Ash 91.05% Sulphur 1.75%

Sulphur distribution in products of distillation

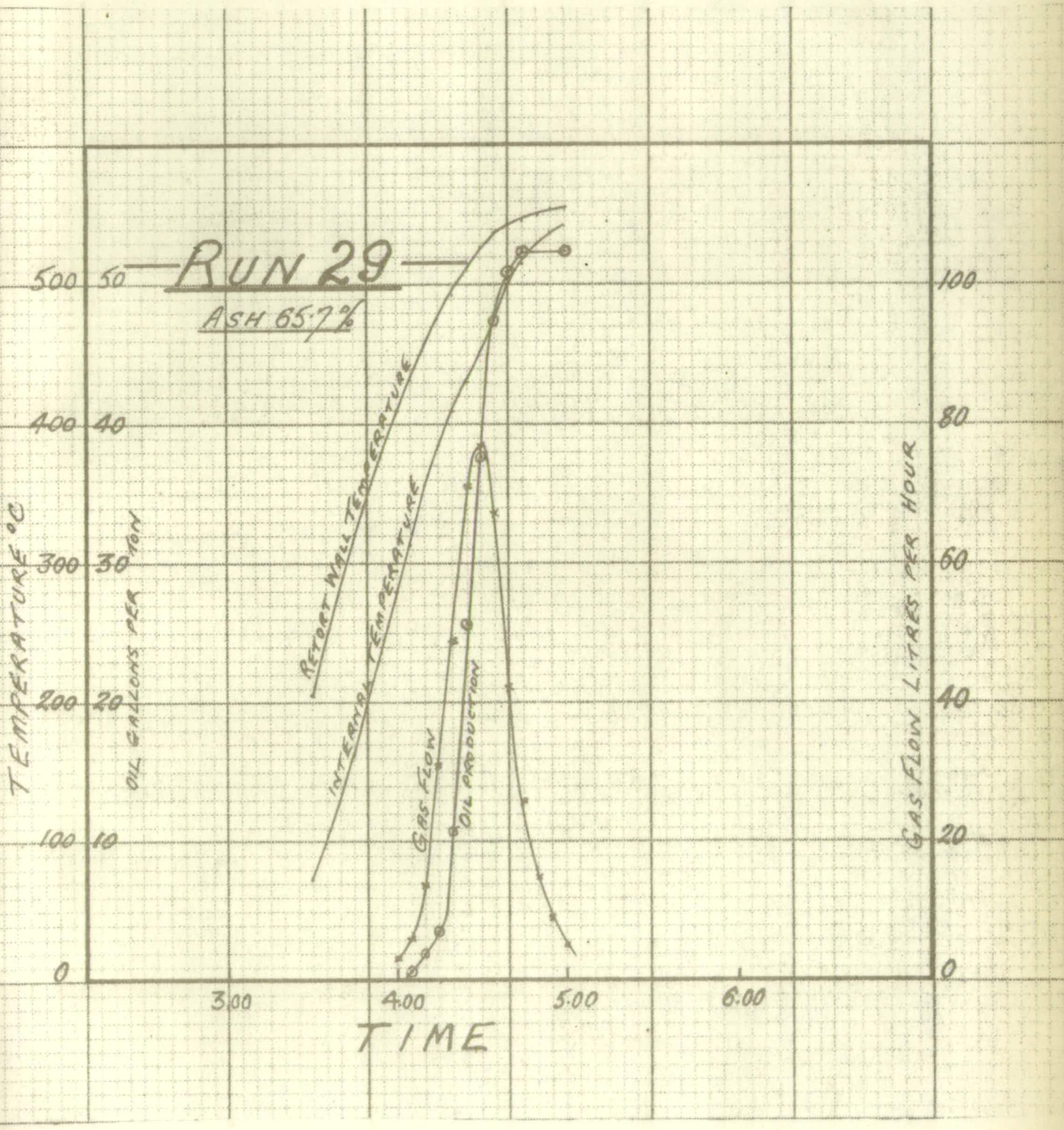
Residue	48.4%
Oil	19.4
Hydrogen sulphide	29.2
Other gases and loss	3.0
	100.0

General Data

Ash/shale ratio		0.657	
Kerogen percentage		34.3%	
Distillation Index		1.53	
Rate of heating in distillation range		280	deg.C/hour
Total time of oil production		0.66	hour
Maximum rate of oil production		166	galls/ton/hour
do. per % kerogen		4.83	do.
Gas production	Carbon dioxide	52	cu.ft./ton N.T.P.
	Hydrogen sulphide	190	do.
	Scrubbed gas	1002	do.
	Total gas	1244	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	65.70	
Volatiles in residue	3.92	11.40%
Fixed carbon in residue	3.03	8.85
Oil	21.75	63.45
Water	2.23	6.50
Carbon dioxide	0.29	0.85
Hydrogen sulphide	0.80	2.30
Other gases and loss	2.28	6.65
	100.00	100.00


RUN 29
ASH 65.7%
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
500
400
300
200
100
0
50
40
30
20
10
100
80
60
40
20
0
3.00
4.00
5.00
6.00

RUN No. 30

Charge 1120 grams standard sample, ash 67.2%, in 3/16" thickness flakes. Distilled moderately slowly.
Oil vapours passed through a cracking tube of 1" internal diameter packed with 370 grams of residue from Run 19 free from fine particles passing a 20 mesh sieve. Length of residue 18 inches. Switched on one heat at 12.00 noon. Room temperature 16 C. Barometer 753 m.m. Gas scrubbed to remove hydrogen sulphide and metered. Oil scrubber catches included in oil yield but not determined separately owing to an accident.

TIME P.M.	RETORT WALL TEMP.	RETORT CENTRE TEMP.	OIL PROD. GALLONS PER TON	GAS FLOW LITRES PER HOUR	CRACKING TUBE TEMP.
12.50	95	37			
2.40	400	333		2.2	
3.00	430	372	1.0	10.0	
3.10				23	595
3.15	450	393	6.4	67	650
3.20	454	400	10.2	80	728
3.25	463	406	11.0	93	743
3.30	468?	410	12.4	101	761
3.35	475	416	13.8	106	761
3.40	480	422	15.4	105	771
3.45	485	428	16.8	104	780
3.50	490	434	18.0	96	780
3.55	496	440	19.4	85	789
4.00	499	448	20.2	75	798
4.05	503	457	21.0	65	798
4.10	506	466	21.2	56	805
4.15	510	474	22.0	49	814
4.30	519	492	22.4	34	817
4.45	501	499	22.6	8.0	705
5.00	468	481	22.6	0	595

Water condensed gallons per ton	6.6
Oil yield gallons per ton	22.6
Specific gravity of oil	0.969
Sulphur content of oil	3.20%
Saturation of oil	28%

Distillation analysis of crude oil 100 m.l.

Up to 150 C	24.0%
150 to 200	13.2
200 to 250	20.3
250 to 300	12.6
Residuum	29.9
	100.0

Run No. 30 continued

Residue

Weight	841 grams	Percentage of shale 75.1%
Gain in weight of residue in cracking tube		14 grams
do. as percentage of shale		1.25%

Proximate analyses	Retort Residue	Cracking Tube Residue
Volatiles	5.70%	3.75%
Fixed carbon	4.75	10.55
Ash	89.55	85.70
Sulphur content	1.88%	1.96%

Sulphur distribution in products of distillation

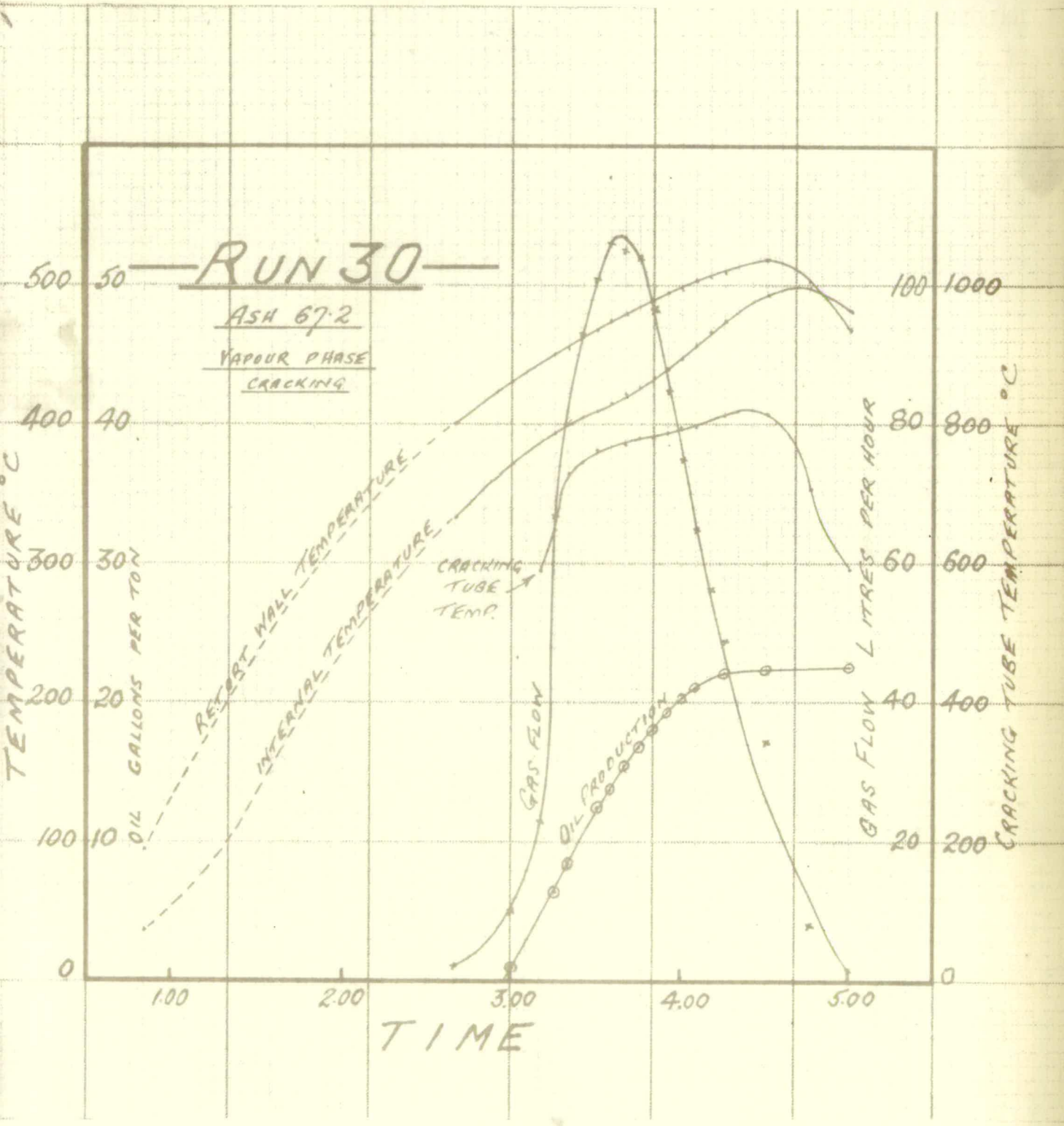
Residue	54.3%
Oil	9.5
Hydrogen sulphide	19.8
Gain in cracking tube	4.4
Other gases and loss	12.0
	100.0

General Data

Ash/shale ratio		0.672	
Kerogen percentage		32.8%	
Distillation Index		0.69	
Rate of heating in distillation range		80	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		23	galls/ton/hour
do. per % kerogen		0.70	do.
Gas production	Carbon dioxide	78	cu.ft./ton N.T.P.
	Hydrogen sulphide	129	do.
	Scrubbed gas	3370?	do.
	Total gas	3577	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	67.25%	
Volatiles in residue	4.28	13.10%
Fixed carbon in residue	3.57	10.90
Gain in cracking tube	1.25	3.80
Oil	9.77	29.85
Water	2.95	9.00
Carbon dioxide	0.43	1.30
Hydrogen sulphide	0.54	1.65
Other gases and loss	9.96	30.40
	100.00	100.00


RUN 30
ASH 67·2
VAPOUR PHASE CRACKING
REKERT WALL TEMPERATURE
INTERNAL TEMPERATURE
CRACKING TUBE TEMP.
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
LITRES PER HOUR
GAS FLOW
CRACKING TUBE TEMPERATURE °C
500
400
300
200
100
0
50
40
30
20
10
100
80
60
40
20
1000
800
600
400
200
0
1.00
2.00
3.00
4.00
5.00
TIME

RUN No. 31

Charge 1120 grams standard sample, 66.6% ash, in 3/16" to ¼" minimum thickness flakes. Distilled moderately slowly. Vapours passed through cracking tube packed in order of gas flow with 150 grams coarse copper turnings and with 100 grams very fine copper turnings.
Switched on one heat at 12.00 noon, cut off 4.30 p.m.
Room temperature 19 C. Barometer 754 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 11 m.l. and 4 m.l. = 3.0 gallons per ton.

TIME P.M.	RETORT WALL TEMP.	RETORT CENTRE TEMP.	OIL PROD. GALLONS PER TON	GAS FLOW LITRES PER HOUR	CRACKING TUBE TEMP.
2.20	398	334		3.0	232
2.30	412	355		5.5	427
2.35				12.0	
2.40	427	372	1.0	33.0	673
2.50				45.0	
3.00	448	400	4.4	106.0	711
3.10	460	410	7.0	114.0	705
3.20	469	421	10.6	97.0	669
3.30	477	431	15.0	81.0	650
3.40	484	443	18.0	76.0	669
3.50	495	459	19.4	62.0	686
4.00	503	475	21.4	45.0	696
4.10	511	488	22.4	30.0	686
4.20	520	501	22.8	20.0	686
4.30	530	508	22.8	14.0	678

Water condensed gallons per ton	5.0
Oil yield gallons per ton	22.8
Specific gravity of oil	0.969
Sulphur content of oil	2.96%
Saturation of oil	26% ?

Distillation analysis of oil 100 m.l.

Up to 150 C	24.0%
150 to 200	18.6
200 to 250	15.7
250 to 300	16.5
Residuum	25.2
	100.0

Residue

Weight 837 grams Percentage of shale 74.75%

Run No. 31 continued

Proximate analysis of residue

Volatiles 5.55% Fixed carbon 5.35% Ash 89.1% Sulphur 1.82%

Sulphur distribution in products of distillation

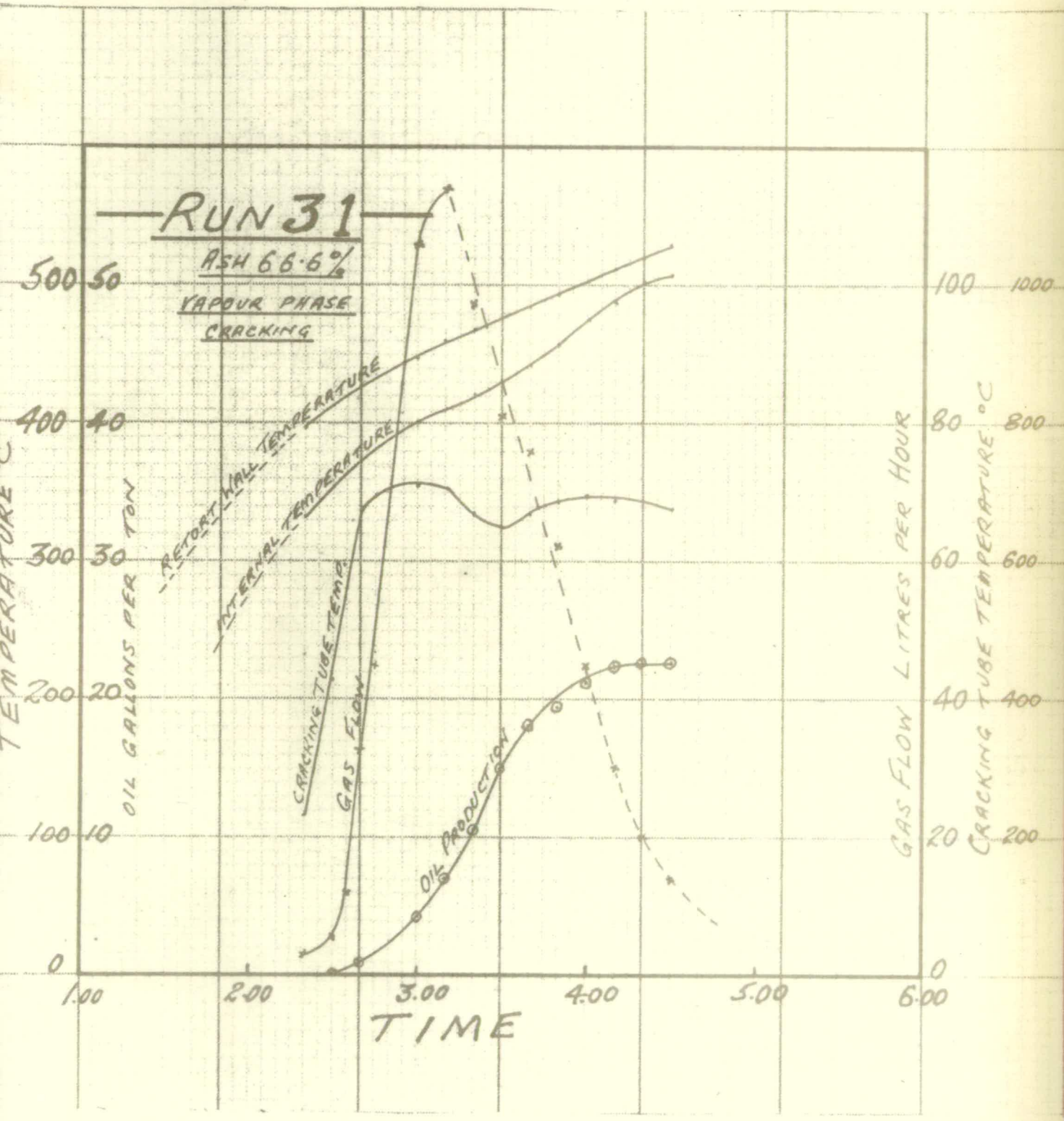
Residue	52.4%
Oil	10.3
Hydrogen sulphide	1.5
Absorbed by copper and loss	35.8
	100.0

General Data

Ash/shale ratio		0.666	
Kerogen percentage		33.4%	
Distillation Index		0.68	
Rate of heating in distillation range		75	deg.C/hour
Total time of oil production		1.75	hours
Maximum rate of oil production		29	galls/ton/hour
do. per % kerogen		0.87	do.
Gas production	Carbon dioxide	62	cu.ft./ton N.T.P.
	Hydrogen sulphide	10	do.
	Scrubbed gas	3840	do.
	Total gas	3912	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.60%	
Volatiles in residue	4.15	12.40%
Fixed carbon in residue	4.00	12.00
Oil	9.86	29.55
Water	2.23	6.65
Carbon dioxide	0.34	1.00
Hydrogen sulphide, gain in C.T. and other gases.	12.82	38.40
	100.00	100.00


RUN 31
ASH 66·6%
VAPOUR PHASE
CRACKING
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
CRACKING TUBE TEMP.
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
CRACKING TUBE TEMPERATURE °C
500
400
300
200
100
0
50
40
30
20
10
100
80
60
40
20
1000
800
600
400
200
1.00
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 32

Charge 1120 grams standard sample, 66.3% ash, in ¼" thickness flakes. Distilled moderately slowly.
Vapours passed through cracking tube containing 300 grams dried shale residue from Run 23.
Switched on one heat at 2.00 p.m. with retort at 120 C and cracking tube at 200 C.
Room temperature 20C. Barometer 763 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 4 m.l. and 2 m.l. = 1.2 gallons per ton.

TIME P.M.	RETORT WALL TEMP.	RETORT CENTRE TEMP.	OIL PROD. GALLONS PER TON	GAS FLOW LITRES PER HOUR	CRACKING TUBE TEMPERATURE
2.15	150	139			280
2.30	194	142			377
2.45	242	164			405
3.00	284	200			427
3.15	324	244			450
3.30	359	283	0.2		453
3.45	390	324	0.4	1.3	456
3.50				2.0	
3.55				3.5	
4.00	416	358	1.2	6.8	458
4.05				10.0	
4.10				13.6	
4.15	440	386	4.0	18.0	460
4.20				21.7	
4.25				25.4	
4.30	465	410	11.4	29.6	462
4.35				31.8	
4.40				32.5	
4.45	487	431	23.0	32.2	460
4.53				30.0	
5.00	509	466	31.8	24.4	460
5.05				21.7	
5.10				17.0	
5.15	528	503	36.4	12.3	460
5.20				10.7	
5.25				8.5	
5.30	548	529	38.2	6.8	465
5.45	561	545	39.0	5.5	467

Water condensed gallons per ton	5.6
Oil yield gallons per ton	39.0
Specific gravity of oil	0.899
Sulphur content of oil	2.32%
Saturation of oil	39%

Run No. 32 continued

Distillation analysis of crude oil	100 m.l.
Up to 150 C	16.3%
150 to 200	13.0
200 to 250	12.2
250 to 300	14.5
Residuum	44.0
	100.0

Residue

Weight 826 grams Percentage of shale 73.8%
Cracking tube residue gain 48 grams Percentage of shale 4.3%

Proximate analyses of residues	Retort residue	C. Tube residue
Volatiles at 900 C.	5.05%	15.6%
Fixed carbon	5.00	5.5
Ash	89.95	78.9
	100.00	100.0
Sulphur content of residue	1.77%	1.72%

Sulphur distribution in products of distillation

Residue	50.2%
Oil	13.4
Hydrogen sulphide	23.4
Gain in cracking tube residue	4.0
Other gases and loss	9.0
	100.0

General Data.

Ash/shale ratio		0.663	
Kerogen percentage		33.7%	
Distillation Index		1.16	
Rate of heating in distillation range		100	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		45	galls/ton/hour
do. per % kerogen		1.33	do.
Gas production	Carbon dioxide	118	cu.ft./ton N.T.P.
	Hydrogen sulphide	153	do.
	Scrubbed gas	1008	do.
	Total gas	1279	do.

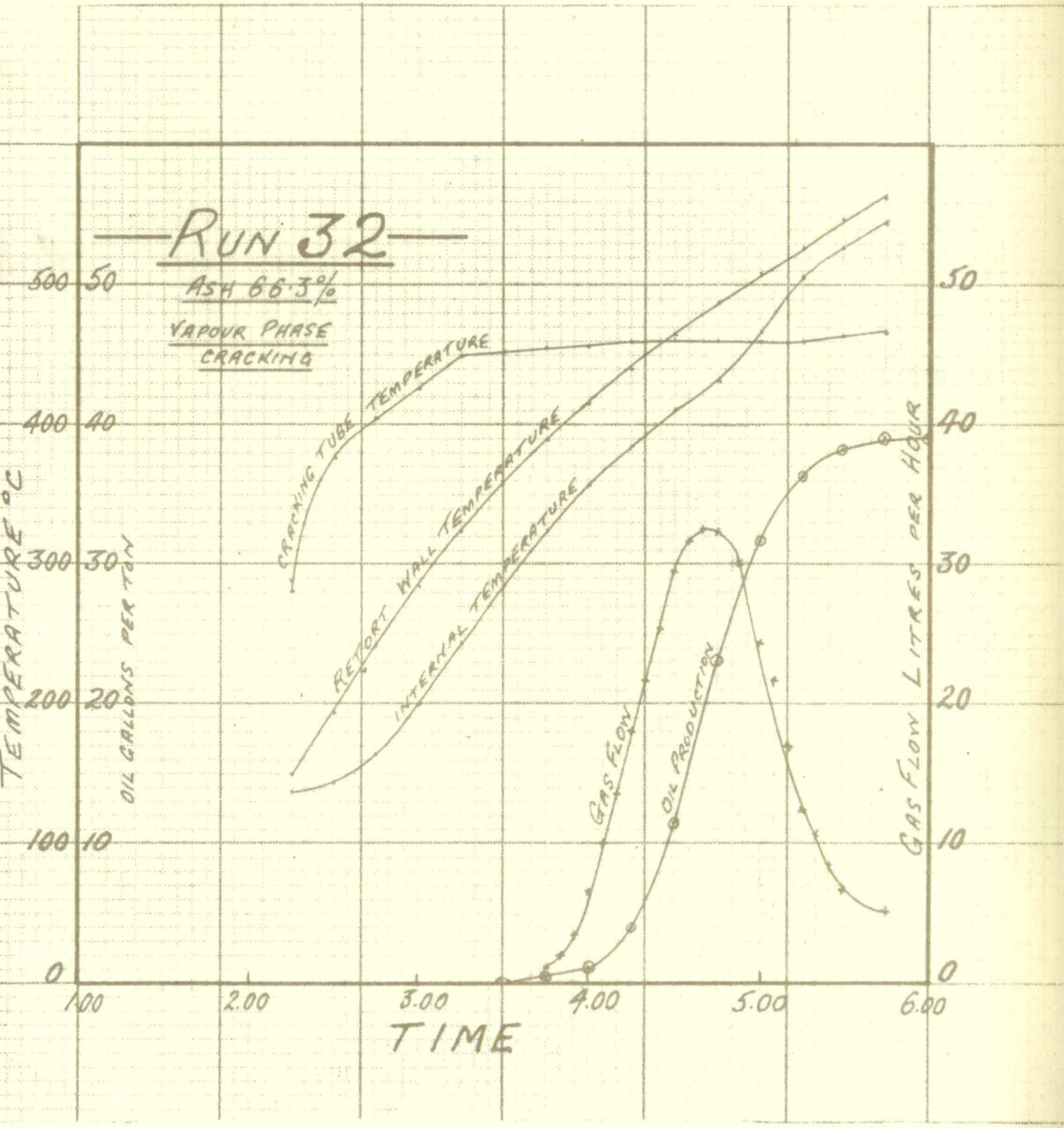
Run No. 32 continued

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.30%	
Volatiles in residue	3.72	11.05%
Fixed carbon in residue	3.68	10.90
Gain in cracking tube	4.28	12.70
Oil	15.65	46.45
Water	2.50	7.40
Carbon dioxide	0.65	1.95
Hydrogen sulphide	0.65	1.95
Other gases and loss	2.57	7.60
	100.00	100.00

General Note

In this run the comparatively low temperature of the cracking tube allowed a little of the heaviest fraction of the oil to remain in the tube at one end which was probably somewhat cooler. The excess gain in weight of the cracking tube would be equivalent to 6 or 8 gallons of oil per ton. The oil yield in this run is thus misleading and should probably be in the region of 45 gallons per ton. Instead of repeating this run a further distillation was made in which the cracking tube was kept about 100 C higher and the results are given in the next result sheet i.e. Run 33.


RUN 32
ASH 66·3%
VAPOUR PHASE CRACKING
CRACKING TUBE TEMPERATURE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 33

Charge 1120 grams standard sample, 66.6% ash, in 3/16" to ¼" thickness flakes. Distlled moderately slowly.
Vapours passed through cracking tube containing 300 grams residue from Run 31 with fines -20 mesh removed.
Switched on one heat at 9.00 a.m. Room temperature 18 C.
Barometer 756 m.m. Gas scrubbed to remove hydrogen sulphide and metered. Oil scrubber catches 3 m.l. and 2 m.l. = 1.0 gall/ton.

TIME	RETORT WALL TEMP.	RETORT CENTRE TEMP.	OIL PROD. GALLONS PER TON	GAS FLOW LITRES PER HOUR	CRACKING TUBE TEMPERATURE
9.30	101	40			540
10.00	210	117			515
10.30	298	210			561
10.45	335	261			558
11.00	368	306		2.0	558
11.15	396	342	1.0	5.0	556
11.23				7.2	
11.30	422	372	2.0	13.0	554
11.35				17.5	
11.40				22.0	
11.45	444	399	6.8	26.5	556
11.50				30.5	
11.55				33.5	
12.00	466	420	15.0	35.3	558
12.15	487	440	24.8	33.8	558
12.30	504	478	29.8	23.0	560
12.45	521	505	32.0	17.0	559
12.50				15.4	
2.20	548	540	34.0	3.5	556
3.00	549	542	34.2	1.3	549

Water condensed gallons per ton	6.0
Oil yield gallons per ton	34.2
Specific gravity of oil	0.892
Sulphur content of oil	2.52%
Saturation of oil	39%

Distillation analysis of crude oil 100 m.l.

Up to 150 C	23.6%
150 to 200	14.0
200 to 250	10.7
250 to 300	18.5
Residuum	33.2
	100.0

Residue

Weight 842 grams Percentage of shale 75.1%

Run No. 33 continued

Gain in cracking tube residue 19 grams Percentage of shale 1.7%

Proximate Analyses	Retort residue	Cracking tube residue
Volatiles	5.80%	8.55%
Fixed carbon	5.65	6.70
Ash	88.55	84.75
Sulphur	1.78%	2.24%

Sulphur distribution in products of distillation

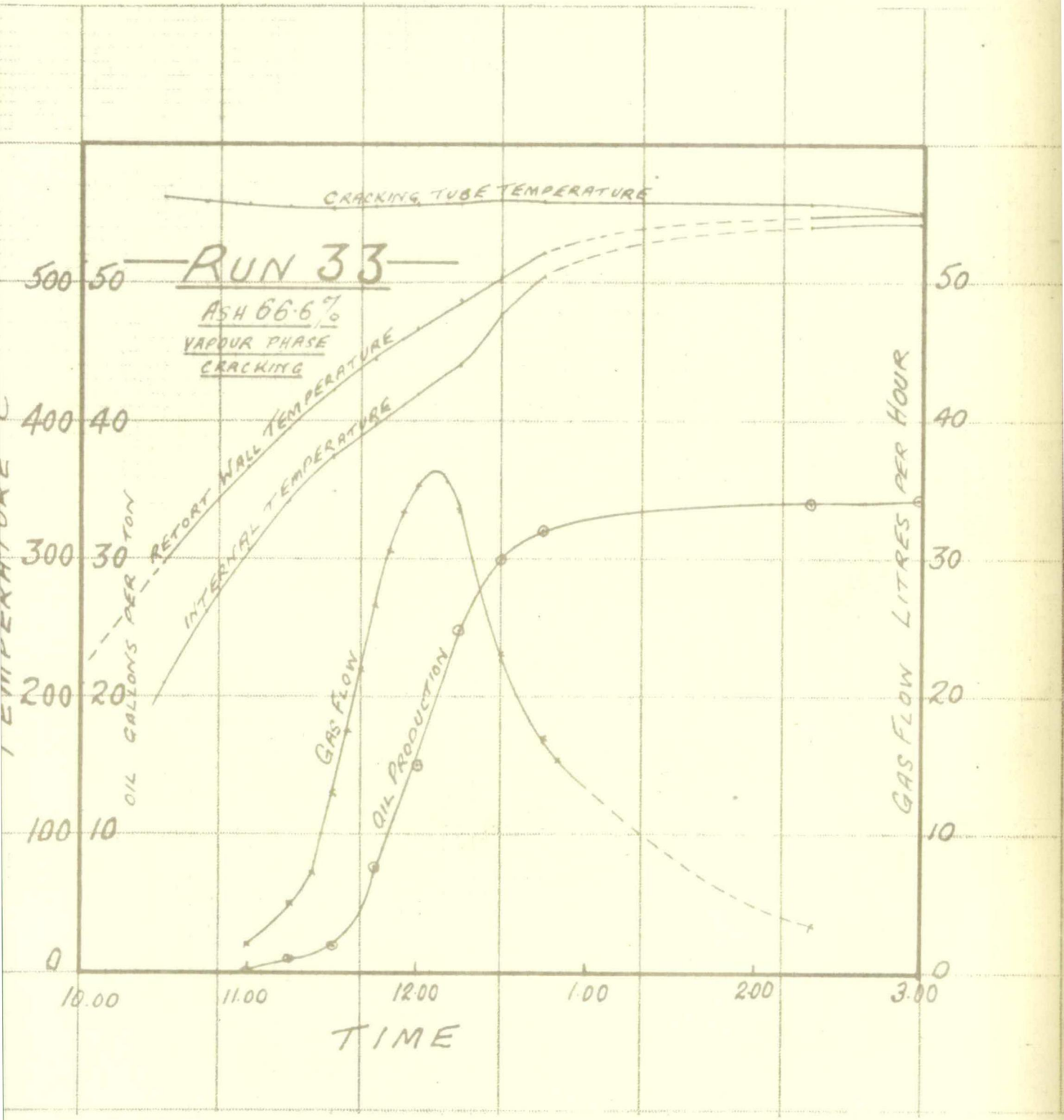
Residue	51.5%
Oil	13.2
Hydrogen sulphide	21.7
Gain in cracking tube	5.8
Other gases and loss	7.8
	100.0

General Data

Ash/shale ratio		0.665	
Kerogen percentage		33.5%	
Distillation Index		1.03	
Rate of heating in distillation range		100	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		35	gallons/ton/hour
do. per % kerogen		1.05	do.
Gas production	Carbon dioxide	149	cu.ft./ton N.T.P.
	Hydrogen sulphide	135	do.
	Scrubbed gas	1481	do.
	Total gas	1765	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.50%	
Volatiles in residue	4.35	13.0%
Fixed carbon in residue	4.25	12.70
Increase in weight cracking tube	1.70	5.05
Oil	13.60	40.60
Water	2.68	8.00
Carbon dioxide	0.82	2.45
Hydrogen sulphide	0.57	1.70
Other gases and loss	5.53	16.50
	100.00	100.00


CRACKING TUBE TEMPERATURE
RUN 33
ASH 66·6 %
VAPOUR PHASE CRACKING
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TEMPERATURE
500
400
300
200
100
0
50
40
30
20
10
0
10.00
11.00
12.00
1.00
2.00
3.00
TIME

RUN No. 34

Charge 1120 grams of a sample from the Australasian Shale Corporation's lease. Ash content 79.9%. Broken to ¼" thickness flakes. This shale appeared to be somewhat weathered.
Switched on one heat at 12.30 p.m. Room temperature 16 C.
Barometer 758 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 2 m.l. and 2 m.l. resp. = 0.8 gallons per ton

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.05	334	269		
2.15	351	295		
2.30	381	338		
2.45	404	364	0.3	
2.50				1.3
2.55			1.0	2.0
3.00	426	390	1.2	6.2
3.15	447	414	3.6	16.7
3.25				24.4
3.30	468	433	10.4	27.3
3.40				27.3
3.45	485	456	17.4	25.4
4.00	503	483	21.4	16.3
4.15	516	503	22.4	10.0
4.30	534	523	23.2	6.8
5.15	565	558	23.6	3.0

Water condensed gallons per ton	4.0
Oil yield gallons per ton	23.6
Specific gravity of oil	0.903
Sulphur content of oil	0.65%
Saturation of oil	50%

Distillation analysis of crude oil 100 m.l.

Up to 150 C	15.8%
150 to 200	9.4
200 to 250	10.0
250 to 300	12.5
Residuum	52.3
	100.0

Residue

Weight 974 grams Percentage of shale 86.9%

Run No. 34 continued

Proximate analysis of residue

Volatiles 4.45% Fixed carbon 3.65% Ash 91.9% Sulphur 0.28%

Sulphur distribution in products of distillation

Residue	79.8%
Oil	20.2
Hydrogen sulphide	0.0
	100.0

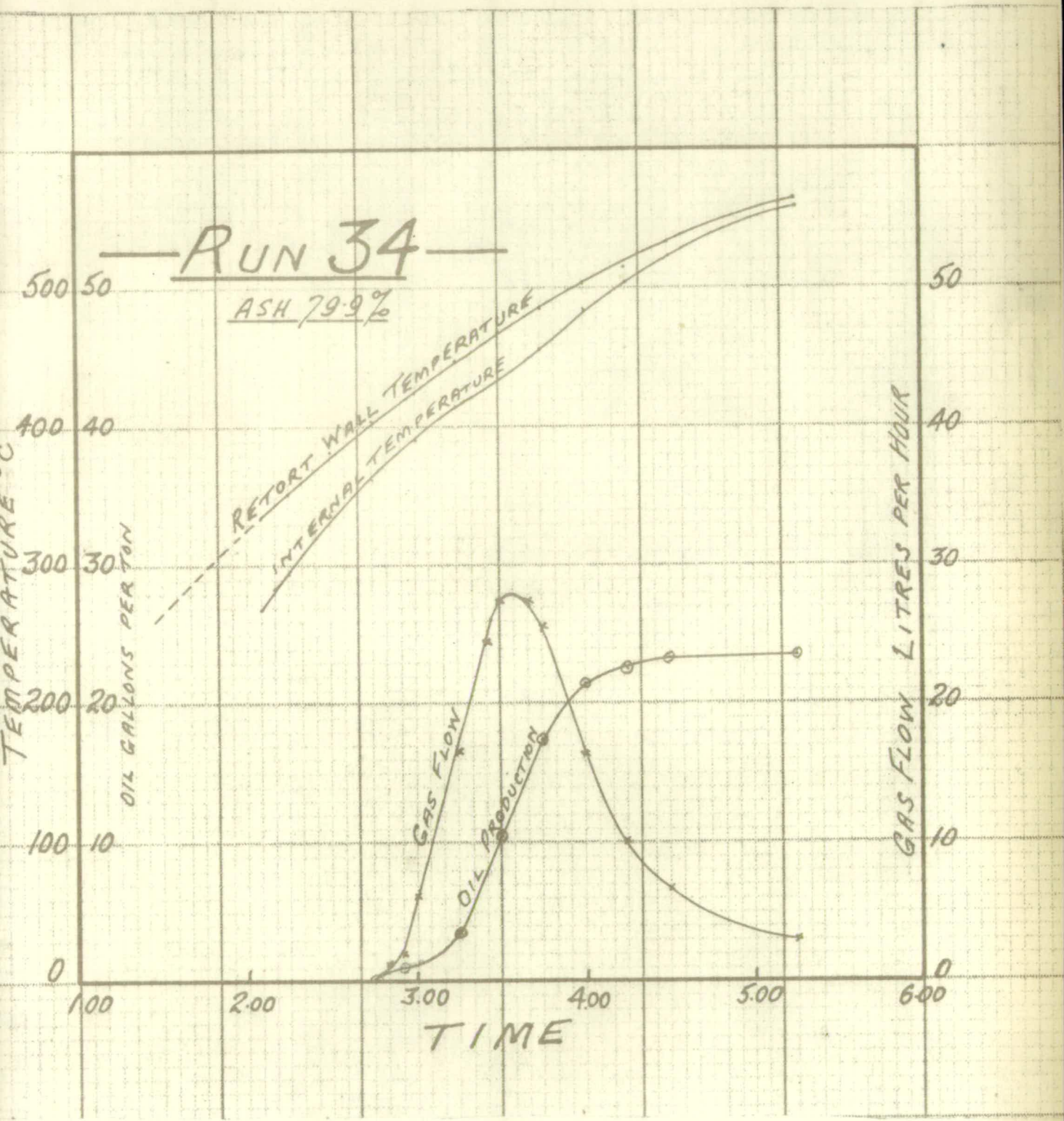
The scrubbed gas on combustion did not produce any sulphur dioxide and was therefore free from sulphur. This is the exception and not the rule. The raw shale contained only 0.30% sulphur.

General Data

Ash/shale ratio		0.799	
Kerogen percentage		20.1%	
Distillation Index		1.17	
Rate of heating in distillation range		95	deg.C/hour
Total time of oil production		1.75	hours
Maximum rate of oil production		29	galls/ton/hour
do. per % kerogen		1.44	do.
Gas production	Carbon dioxide not detd.		
	Hydrogen sulphide nil		
	Scrubbed gas	925	cu.ft./ton N.T.P.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	79.9	
Volatiles in residue	3.87	19.25%
Fixed carbon in residue	3.18	15.80
Oil	9.52	47.35
Water	1.78	8.85
Gases and loss	1.75	8.75
	100.00	100.00


RUN 34
ASH 79.9%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 35

Charge 1680 grams of middle band from the Tasmanite Shale Oil Company's property, ash content 90.6%, crushed to approximately ½" size. Room temperature 15 C. Barometer 772 m.m.
Switched on one heat at 12.30 p.m., cut off at 5.00 p.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 0.5 m.l. and 0.5 m.l. = 0.14 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.15	336	259		
2.30	361	294		
2.45	386	328		0.5
2.55				1.5
3.00	411	361	0.5	3.5
3.15	433	386	1.1	5.0
3.20				6.2
3.25				6.8
3.30	453	406	3.5	8.0
3.40				8.2
3.45	468	424	5.0	8.0
4.00	486	446	5.5	6.2
4.15	503	468	6.3	3.5
4.30	515	486	6.4	1.3
5.00	542	519	6.4	

Water condensed gallons per ton	2.8
Oil yield gallons per ton	6.4
Specific gravity of oil	0.909
Sulphur content of oil	2.28%
Saturation of oil	34%

Distillation analysis not determined as the crude oil was barely sufficient in quantity.

Residue

Weight 1591 grams Percentage of shale 94.75%

Proximate Analysis of residue

Volatiles 3.5% Fixed carbon 0.9% Ash 95.6% Sulphur 2.12%

Run No. 35 continued

Sulphur distribution in products of distillation

Recovery as in residue	33.8	grams
Oil	1.0	
Hydrogen sulphide	9.5	
Total recovery	44.3	grams

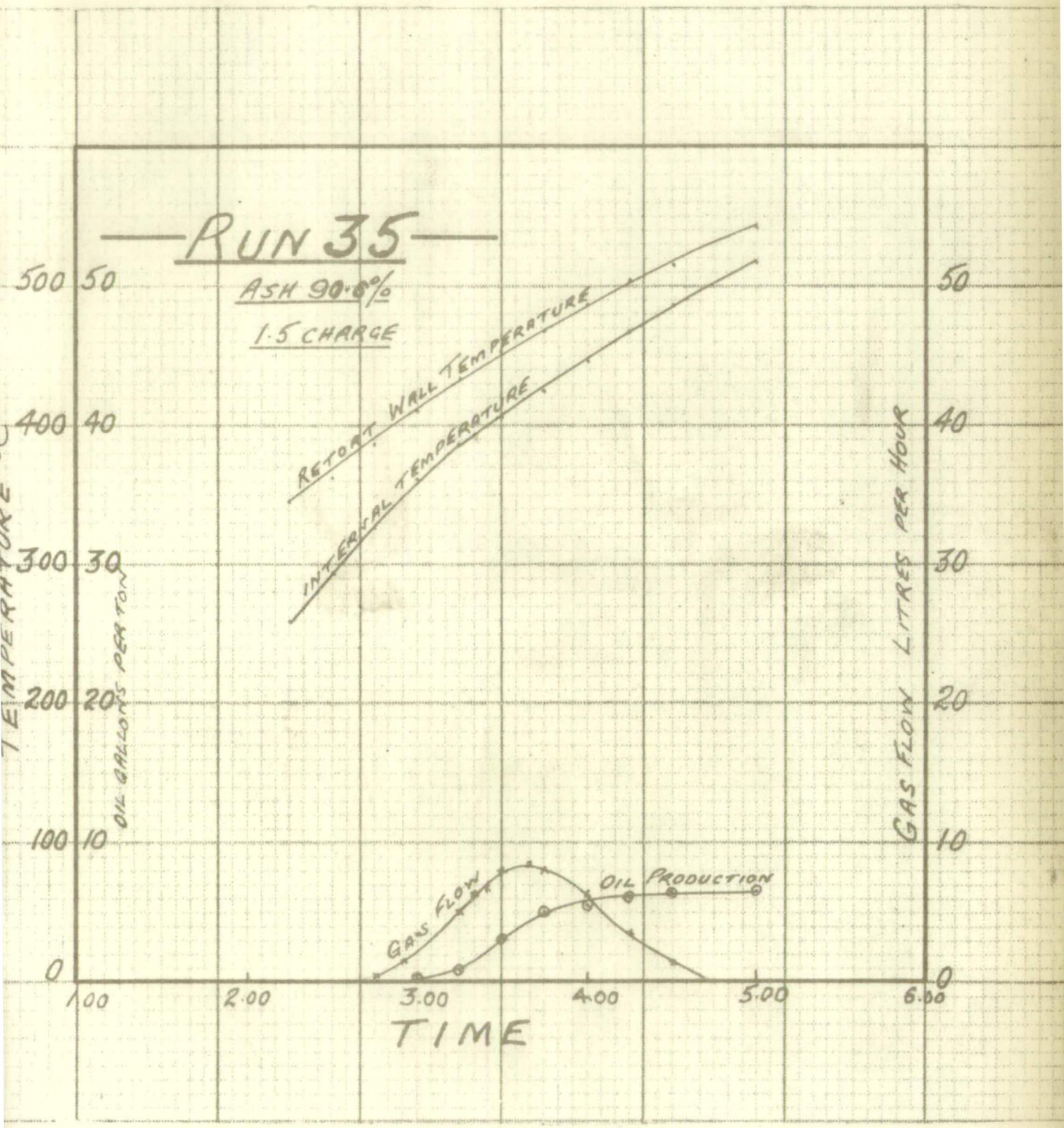
The sulphur content of the shale was not determined but the recovered sulphur amounts to 2.64% of the shale.

General Data.

Ash/shale ratio		0.906	
Kerogen percentage		9.4%	
Distillation Index		0.68	
Rate of heating in distillation range		80	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		10	galls/ton/hour
do. per % kerogen		1.12	do.
Gas production	Carbon dioxide	67	cu.ft./ton N.T.P.
	Hydrogen sulphide	142	do.
	Scrubbed gas	186	do.
	Total gas	395	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	90.6%	
Volatiles in residue	3.30	35.05
Fixed carbon in residue	0.85	9.05
Oil	2.59	27.55
Water	1.25	13.30
Carbon dioxide	0.37	3.95
Hydrogen sulphide	0.60	6.40
Other gases and loss	0.44	4.70
	100.00	100.00


RUN 35
ASH 90·6%
1·5 CHARGE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
GAS FLOW
OIL PRODUCTION
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 36

Charge 1680 grams very poor middle band from Tasmanite Shale Oil Company's property, 93.5% ash, crushed to ¼" size.
Switched on one heat at 2.30 p.m. after preliminary warming up.
Room temperature 16 C. Barometer 772 m.m.
Gas scrubbed from hydrogen sulphide and metered
Oil scrubber catches total 1.0 m.l. = 0.1 gallon per ton approx.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.45	187	187		
3.00	228	187		
3.15	263	208		
3.30	301	244		
3.45	330	279		
4.00	357	310		
4.15	386	342		
4.30	410	371	0.1	1.5
4.40				3.5
4.45	431	395	0.6	5.0
5.00	449	418	1.5	5.5
5.15	469	437	2.1	5.0
5.30	487	461	2.6	3.0
5.45	507	480	2.6	1.5
6.00	522	499	2.7	0.8

Water condensed gallons per ton	1.5
Oil yield gallons per ton	2.7
Specific gravity of oil	0.911
Sulphur content of oil	2.48%
Saturation of oil	40%

Distillation analysis of oil not determined.

Residue

Weight 1636 grams Percentage of shale 97.5%

Proximate analysis of residue

Volatiles plus fixed carbon 3.9% Ash 96.1% Sulphur 1.79%

Run No. 36 continued

Sulphur recovery in products of distillation

Recovery in residue	29.25 grams
Oil	0.30
Hydrogen sulphide	4.2
Total recovery	33.75 grams

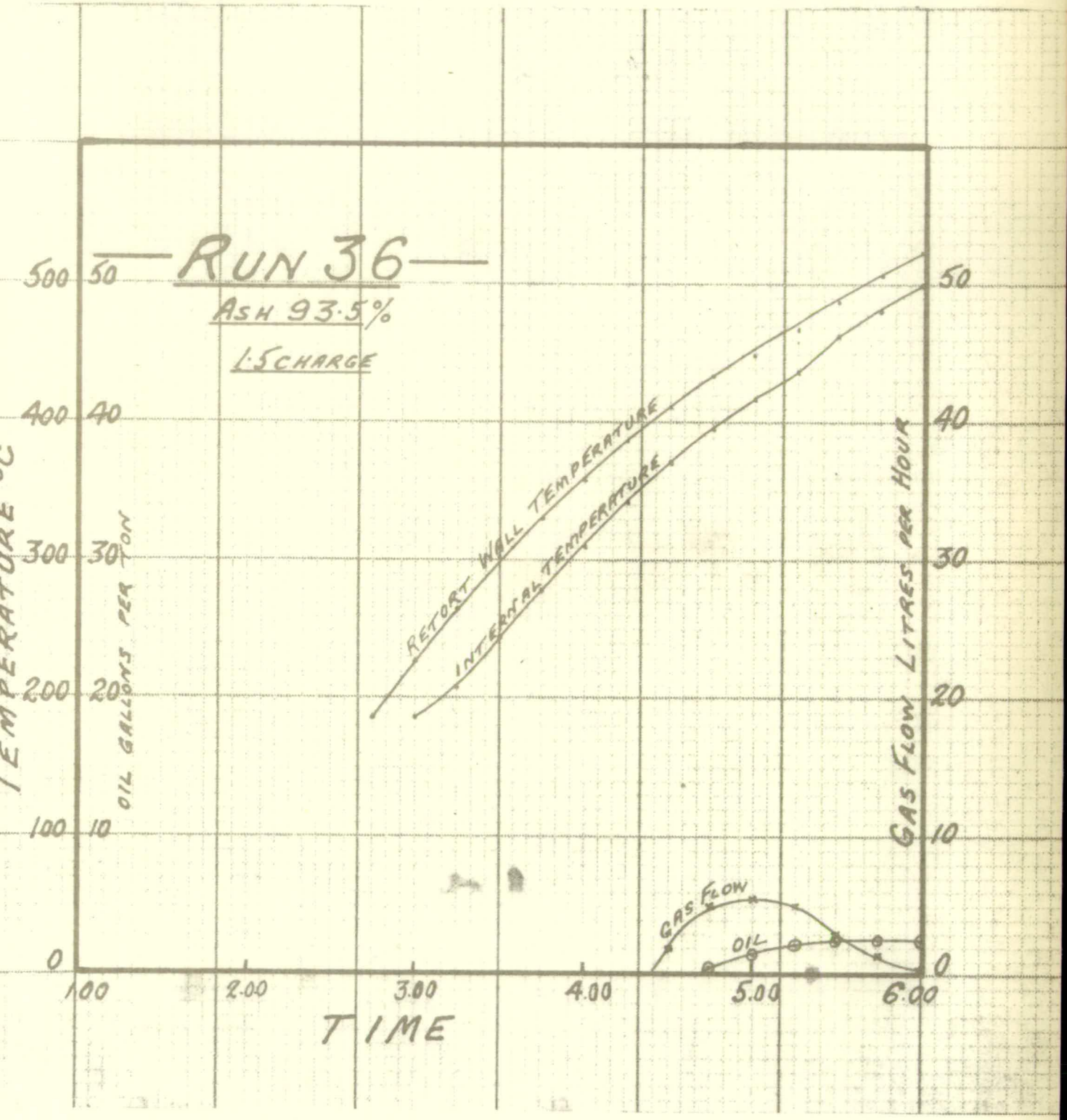
The sulphur content of the shale was not determined but the recovered sulphur amounts to 2.01% of the shale charged.

General Data

Ash/shale ratio		0.935	
Kerogen percentage		6.5%	
Distillation Index		0.41	
Rate of heating in distillation range		85	deg.C/hour
Maximum rate of oil production		5	galls/ton/hour
do. per % kerogen		0.77	do.
Total time of oil production		1.0	hour
Gas production	carbon dioxide	70	cu.ft./ton N.T.P.
	Hydrogen sulphide	62	do.
	Scrubbed gas	106	do.
	Total gas	238	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	93.50	
Volatiles in residue	3.90	60.00%
Fixed carbon in residue	-- --	-- --
Oil	1.10	16.90
Water condensed	0.67	10.30
Carbon dioxide	0.39	6.00
Hydrogen sulphide	0.26	4.05
Other gases and loss	0.18	2.75
	100.00	100.00


RUN 36
ASH 93·5%
1·5 CHARGE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 37

Charge 1120 grams of shale taken from retort feed at the Tasmanite Shale Oil plant in May 1930, ash 68.3%, in ¼" thickness flakes. Room temperature 16 C. Barometer 766 m.m.
Switched on one heat 10.30 a.m., cut off 3.15 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 and 2 m.l. respectively = 1.0 gallon per ton

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.00	283	197		
12.15	316	236		
12.30	348	277	0.2	
12.45	374	316	0.8	1.0
1.00	402	349	2.0	5.0
1.10				6.8
1.15	424	374	4.4	8.5
1.23				11.3
1.30	445	398	10.4	15.0
1.37				18.0
1.45	463	414	19.4	21.4
1.55				23.0
2.00	480	432	30.4	23.0
2.07				21.8
2.15	495	458	38.0	18.5
2.27				15.7
2.30	509	482	42.0	12.5
2.40				10.0
2.45	522	503	43.6	8.5
2.55				7.3
3.00	532	520	44.4	6.8
3.10				5.5
3.15	542	531	45.2	5.5
3.30	521	532	45.4	2.0

Water condensed gallons per ton	3.4
Oil yield gallons per ton	45.4
Specific gravity of oil	0.910
Sulphur content of oil	2.53%
Saturation of oil	34%

Distillation analysis of crude oil 100 m.l.

Up to 150 C	12.5%
150 to 200	11.6
200 to 250	10.6
250 to 300	13.3
Residuum	52.0
	100.0

Run No. 37 continued

Residue

Weight 856 grams Percentage of shale 76.5%

Proximate analysis of residue

Volatiles 4.8% Fixed carbon 5.9% Ash 89.3% Sulphur 1.74%

Sulphur distribution in products of distillation

Recovery in residue	14.9 grams
Oil	5.2
Hydrogen sulphide	12.2
Total recovery	32.3 grams

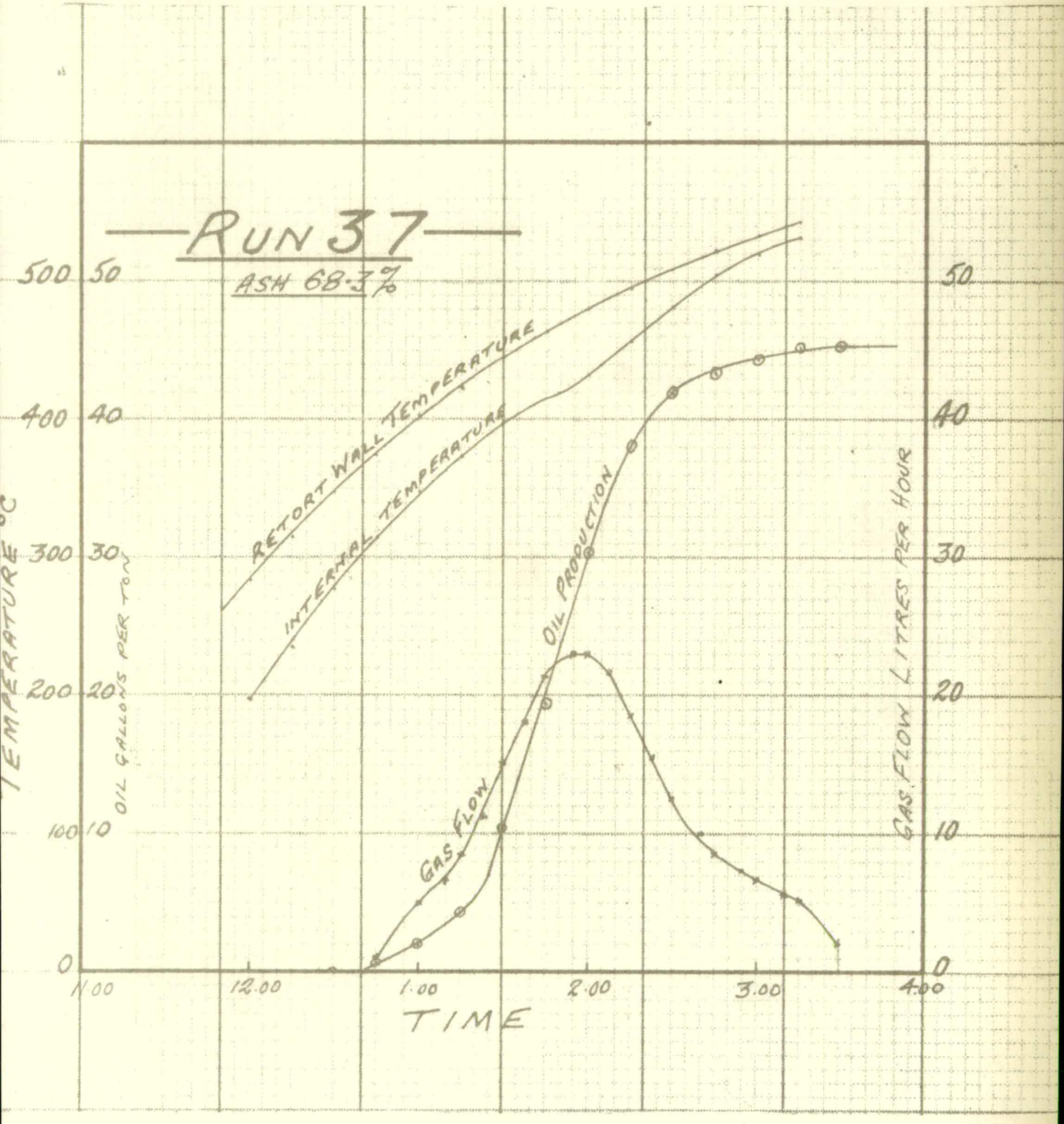
Sulphur content of shale not determined.

General Data

Ash/shale ratio		0.683	
Kerogen percentage		31.7%	
Distillation Index		1.43	
Rate of heating in distillation range		80	deg.C/hour
Total time of oil production		2.5	hours
Maximum rate of oil production		40	galls/ton/hour
do. per % kerogen		1.26	do.
Gas production	Carbon dioxide	49	cu.ft./ton N.T.P.
	Hydrogen sulphide	274	do.
	Scrubbed gas	250	do.
	Total gas	1273	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	68.30%	
Volatiles in residue	3.67	11.55%
Fixed carbon in residue	4.51	14.20
Oil	18.40	58.10
Water condensed	1.52	4.80
Carbon dioxide	0.27	0.85
Hydrogen sulphide	1.16	3.65
Other gases and loss	2.17	6.85
	100.00	100.00


RUN 37
ASH 68·3%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00

RUN No. 38

Charge 1120 grams of richest available shale from the Tasmanite Shale Oil Co, ash 61.9%, in ¼" thickness flakes.
Room temperature 15 C. Barometer 760 m.m.
Switched on one heat at 12.15 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 2 m.l. and 2 m.l. respectively = 0.8 gall/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.05	353	281	0.4	1.3
2.15	370	302	1.0	4.1
2.30	397	335	2.0	5.5
2.37				6.8
2.45	420	361	5.0	8.5
2.54				11.3
3.00	438	384	10.2	15.0
3.09				17.0
3.15	457	400	21.2	19.4
3.24				21.7
3.30	474	418	38.6	23.0
3.38				23.0
3.45	492	433	52.4	22.2
3.54				19.4
4.00	505	460	61.0	17.5
4.09				14.0
4.15	521	490	64.0	13.2
4.22				9.6
4.30	534	513	64.8	7.8
4.45	548	530	65.0	5.0

Water condensed gallons per ton	2.2
Oil yield gallons per ton	65.0
Specific gravity of oil	0.913
Sulphur content of oil	2.51%
Saturation of oil	32%

Distillation analysis of oil 100 m.l.

Up to 150 C	10.9%
150 to 200	10.5
200 to 250	10.7
250 to 300	11.8
Residuum	56.1
	100.0

Residue

Weight 767 grams Percentage of shale 68.5%

Run No. 38 continued

Proximate analysis of residue

Volatiles 4.75% Fixed carbon 4.80% Ash 90.45% Sulphur 1.11%

Sulphur distribution in products of distillation

Recovery in residue	8.45 grams
Oil	7.45
Hydrogen sulphide	13.40
	29.30 grams

The sulphur content of the shale was not determined as previous work had shown almost complete recovery of sulphur, the only exception being in those cases where the gas still contains a little sulphur not removable by alkali scrubbing.

General Data

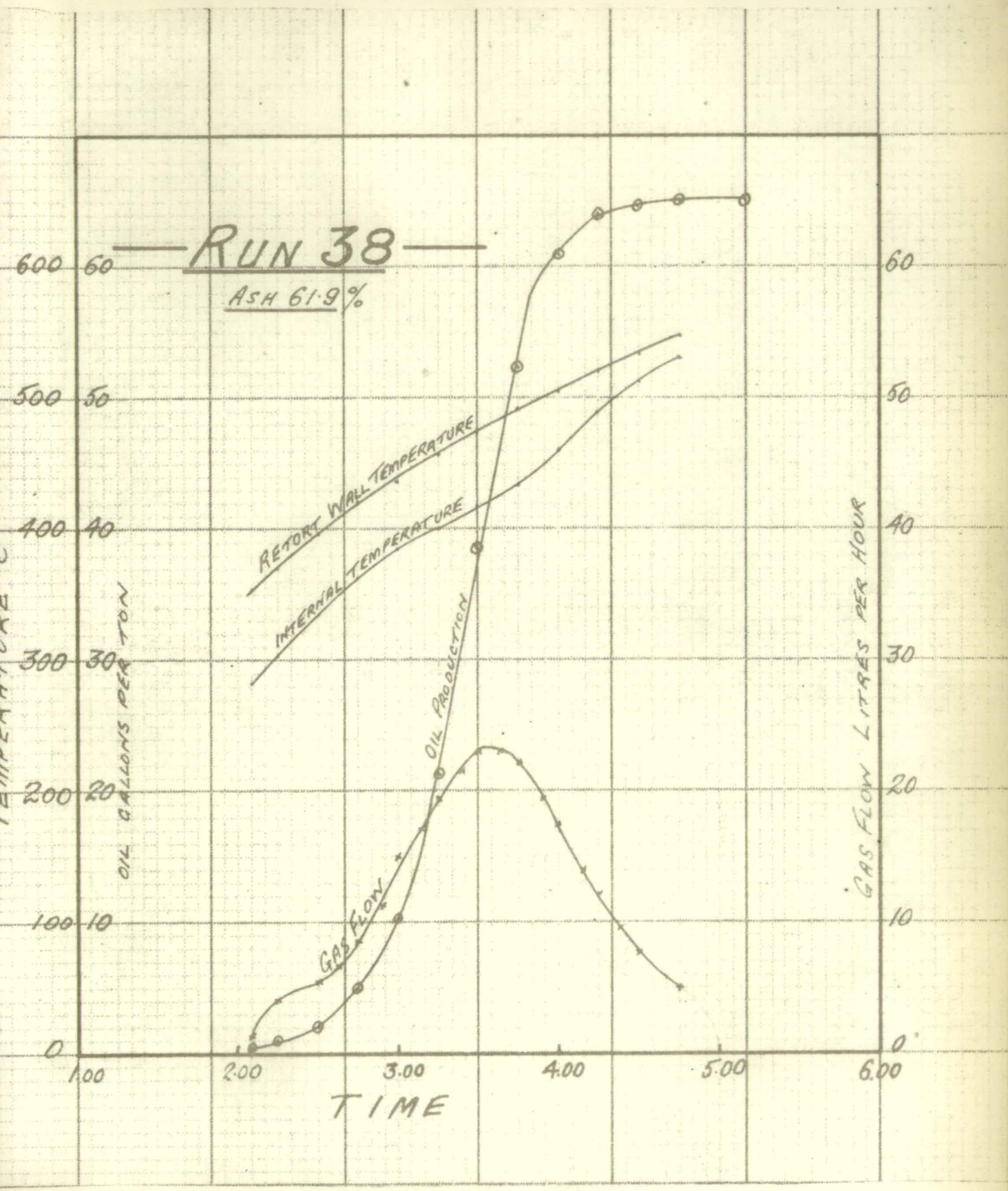
Ash/shale ratio		0.619	
Kerogen percentage		38.1%	
Distillation Index		1.70	
Rate of heating in distillation range		80	deg.C/hour
Maximum rate of oil production		62	galls/ton/hour
do. per % kerogen		1.62	do.
Total time of oil production		2.5	hours
Gas production	Carbon dioxide	48	cu.ft./ton N.T.P.
	Hydrogen sulphide	300	do.
	Scrubbed gas	1085	do.
	Total gas	1433	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	61.90%	
Volatiles in residue	3.26	8.55%
Fixed carbon in residue	3.28	8.60
Oil	26.50	69.55
Water condensed	0.98	2.55
Carbon dioxide	0.26	0.70
Hydrogen sulphide	1.27	3.35
Other gases and loss	2.55	6.70
	100.00	100.00

Note

Subsequent determination of the sulphur content of the shale showed it to be 2.69%. making the total weight of sulphur present 30.15 grams. The Other gases and loss item is therefore 2.8%, residue 27.9%, oil 24.7%, hydrogen sulphide 44.6%.


RUN 38
ASH 61·9%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
TEMPERATURE
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
600
500
400
300
200
100
0
60
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 39

Charge 1120 grams survey sample 8A, bottom seam Goliath Portland Cement Co's mine, New Tunnel, ash 83.5% in ¼" to ⅛" flakes and down to dust.
Switched on one heat at 12.30 p.m.
Room temperature 12 C. Barometer 750 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 2 m.l. and 1 m.l. respectively = 0.6 gall/to

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOU
2.30	342	264		
2.45	370	304	0.2	
3.00	396	340	0.4	3.0
3.15	419	368	1.2	5.0
3.30	435	392	4.0	8.0
3.45	452	411	8.8	10.8
4.00	468	428	11.6	10.8
4.15	480	448	13.4	8.5
4.30	492	468	15.2	6.8
4.45	505	483	15.8	3.5
5.00	517	501	16.2	2.0
5.30	540	525	16.2	1.5

Water condensed gallons per ton	4.6
Oil yield gallons per ton	16.2
Specific gravity of oil	0.922
Sulphur content of oil	2.50%
Saturation of oil	36%

Distillation Analysis of oil not determined.

Residue

Weight 999 grams Percentage of shale 89.15%

Proximate Analysis of residue

Volatiles 3.5% Fixed carbon 2.8% Ash 93.7% Sulphur 1.52%

Sulphur distribution in products of distillation

Residue	50.4%
Oil	6.0
Hydrogen sulphide	29.2
Other gases and loss	14.4%
	100.0

Sulphur content of shale sample 2.69% Mines Dept. assay

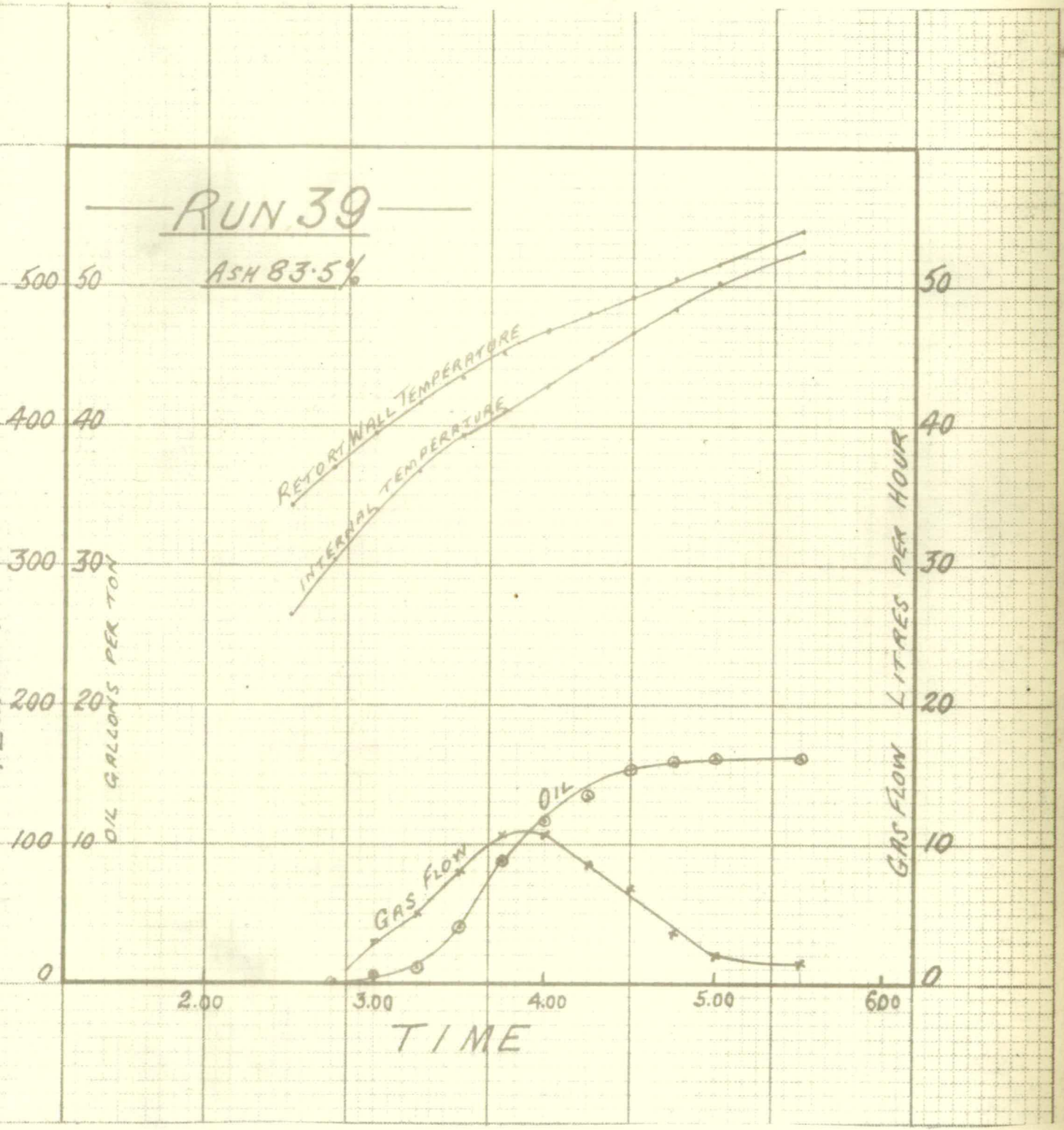
Run No. 39 continued

General Data

Ash/shale ratio		0.835	
Kerogen percentage		16.5	
Distillation Index		0.98	
Rate of heating in distillation range		80	deg.C/hour
Maximum rate of oil production		18	galls/ton/hour
do. per % kerogen		1.09	do.
Total time of oil production		2.0	hours
Gas production	Carbon dioxide	41	cu.ft./ton N.T.P.
	Hydrogen sulphide	197	do.
	Scrubbed gas	469	do.
	Total gas	707	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	83.50%	
Volatiles in residue	3.12	18.90%
Fixed carbon in residue	2.50	15.15
Oil	6.61	40.10
Water condensed	2.05	12.45
Carbon dioxide	0.23	1.35
Hydrogen sulphide	0.83	5.05
Other gases and loss	1.16	7.00
	100.00	100.00


RUN 39
ASH 83·5%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL
GAS FLOW
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 40

Charge 1680 grams survey sample 8B, middle band Goliath Portland Cement Co's mine, New Tunnel, ash 84.5%, size ½" down to dust.
Switched on one heat at 12.10 p.m.
Room temperature 9 C. Barometer 759.m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 7.5 m.l.and 1.0 m.l.resp. = 1.1 galls/ton.
This run was interfered with by furnace burning out but was continued by temporarily connecting up again.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
3.15	291	217		
3.30	346	244	0.4	0.7
3.45	386	271	0.7	2.0
4.00	422	306		5.0
4.15	457	346	3.5	11.8
4.30	486	375	6.2	13.6
4.45	511	400	8.7	13.0
5.00	536	429	9.6	13.0
5.15	558	463	10.4	13.0
5.30	580	492	11.0	13.6
5.45	572	512	11.6	
7.00			12.1	

	Run 40	Run 40A
Water condensed gallons per ton	4.6	5.0
Oil yield gallons per ton	12.1	16.5
Specific gravity of oil	0.935	0.921
Sulphur content of oil		2.50%
Saturation of oil		31%

Distillation analysis of oil not determined

Residue Data	Run 40	Run 40A
Weight	1525 grams	977 grams/1085
Percentage of shale	90.8%	90.0%

Proximate analysis

Volatiles	4.15%	
Fixed carbon	2.65	
Ash	93.20	95.05%
Sulphur	1.78%	1.66%

Run No. 40 continued

Sulphur distribution in products of distillation Run 40A

Residue	53.0%
Oil	6.0
Hydrogen sulphide	26.1
Other gases and loss	14.9
	100.0

Sulphur content of shale 2.82% Mines Dept. Assay
A check assay of the only portion of this sample left gave lower results so that the Loss item was reduced to 1%.

General Data Run 40A

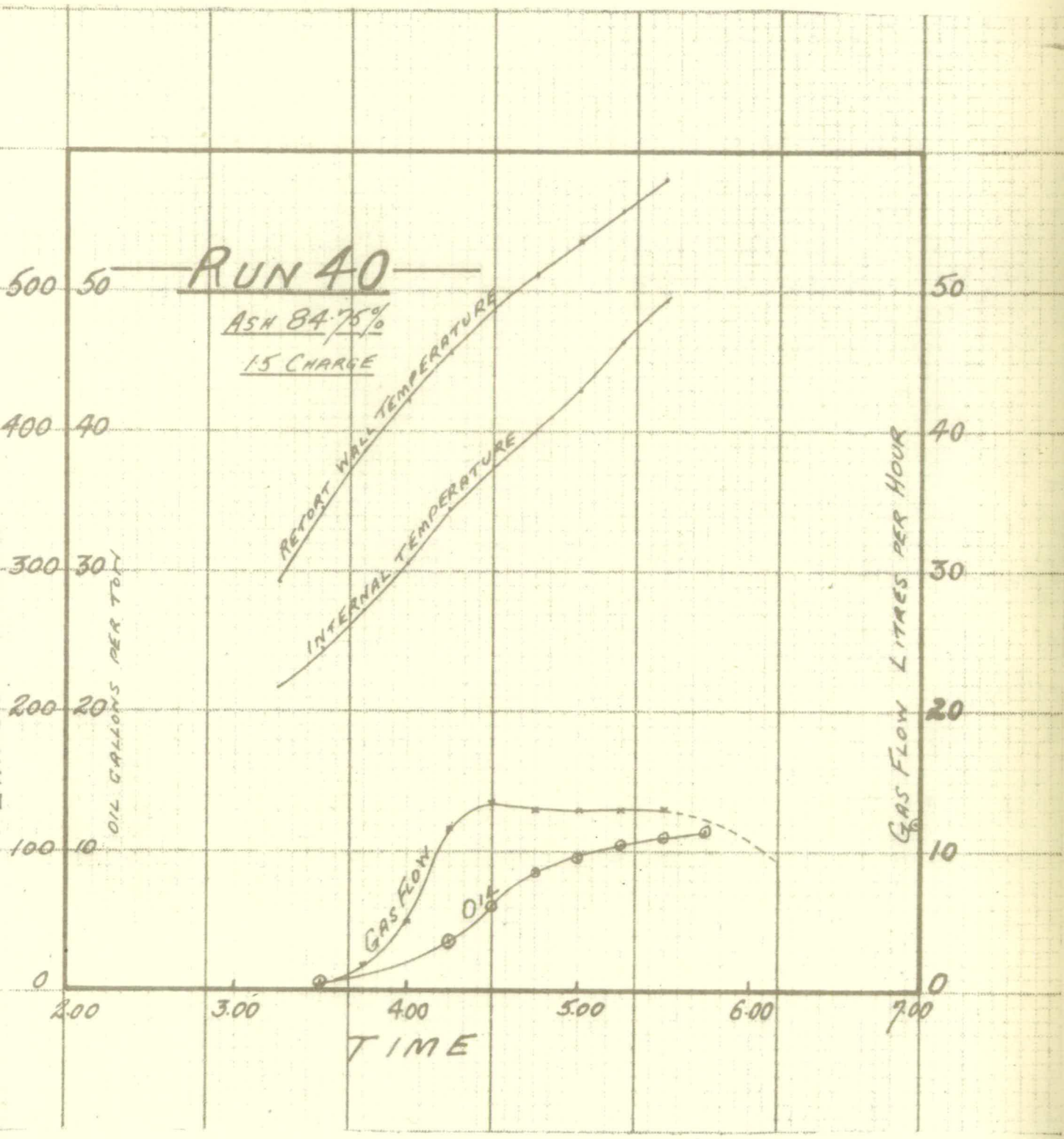
Ash/shale ratio	0.845
Kerogen percentage	15.5%
Distillation Index	1.06

Gas production Run 40	Carbon dioxide	37	cu.ft./ton N.T.P.
	Hydrogen sulphide	185	do.
	Scrubbed gas	587	do.
	Total gas	809	do.

Weight Balance on products of distillation Run 40A

	Percentage of shale	On ashless basis
Ash	84.5 %	
Volatiles plus fixed carbon	4.5	29.00%
Oil	6.79	43.80
Water condensed	2.23	14.40
Carbon dioxide	0.20	1.30
Hydrogen sulphide	0.78	5.05
Other gases and loss	1.00	6.45
	100.00	100.00

The remaining figures are of little value as in Run 40 the retort was inadvertently placed out of its usual position in the furnace and one end was rather cool resulting in the prolonging of distillation and rather incomplete retorting of one end of the charge. The general value of the data is also thus diminished. In addition the spiral oil separator was broken and could not be repaired during the run so that its work was thrown on to the first oil scrubber. Run 40A was carried out to determine the oil yield on the remainder of the sample but no continuous figures were recorded owing to pressure of time. However the figures given in places relating to Run 40A are believed to represent the behaviour of the shale on retorting more closely than those of Run 40 and thus are included.


RUN 40
ASH 84·75%
15 CHARGE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
600
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00
7.00
TIME

RUN No. 41

Charge 1120 grams survey sample 8C, top seam Goliath Portland Cement Co's mine, New Tunnel, ash 70.0%, size ½" down to dust.
Switched on one heat at 12.30 p.m. and put retort in hot furnace at 2.30 p.m. Cut off 7.00 p.m.
Room temperature 10 C. Barometer 745 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 2 m.l. and 2 m.l. respectively= 0.8 gall/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
3.00	305	156		
3.15	335	211		
3.30	361	253	0.2	0.7
3.45	386	293	0.6	3.0
4.00	409	328	2.0	5.5
4.15	425	352	5.2	10.0
4.30	439	374	11.4	16.0
4.45	455	391	19.4	21.7
5.00	468	403	27.4	23.0
5.15	480	418	36.0	21.7
5.30	496	440	41.2	15.0
5.45	510	468	43.2	9.5
7.00	564	539	44.0	0.2

Water condensed gallons per ton	4.6
Oil yield gallons per ton	44.0
Specific gravity of oil	0.915
Sulphur content of oil	2.36%
Saturation of oil	31%

Distillation analysis of oil not determined

Residue data

Weight 859 grams Percentage of shale 76.6%

Proximate analysis of residue

Volatiles 3.6% Fixed carbon 5.0% Ash 91.4% Sulphur 1.86%

Sulphur distribution in products of distillation

Residue	16.0 grams
Oil	4.75
Hydrogen sulphide	10.95
Sulphur accounted for	31.7 grams or 2.83% of the shale.

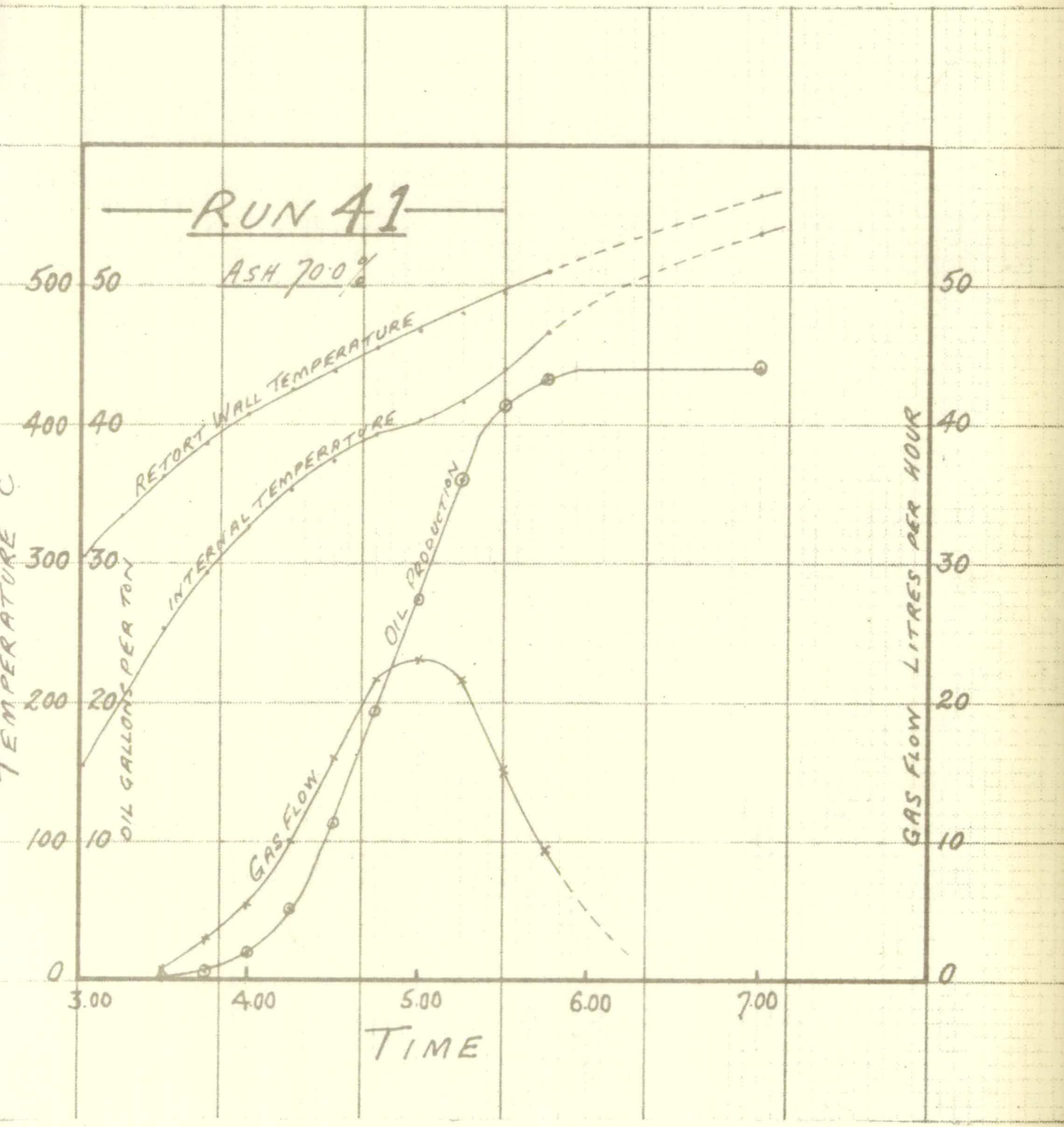
Run No. 41 continued

General Data

Ash/shale ratio		0.700	
Kerogen percentage		30.0%	
Distillation Index		1.47	
Rate of heating in distillation range		70	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		33	galls/ton/hour
do. per % kerogen		1.10	do.
Gas production	Carbon dioxide	75	cu.ft./ton N.T.P.
	Hydrogen sulphide	245	do.
	Scrubbed gas	951	do.
	Total gas	1271	do.

Weight balance on products of distillation

	Percentage of shale	On ashless basis
Ash	70.00%	
Volatiles in residue	2.76	9.20%
Fixed carbon in residue	3.83	12.75
Oil	17.96	59.85
Water condensed	2.05	6.85
Carbon dioxide	0.41	1.40
Hydrogen sulphide	1.04	3.45
Other gases and loss	1.95	6.50
	100.00	100.00


RUN 41
ASH 70.0%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
TEMPERATURE C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
3.00
4.00
5.00
6.00
7.00

RUN No. 42

Charge 1120 grams survey sample 3A, bottom seam, Goliath Portland Cement Co's mine, New Tunnel, ash 75.3%, size ½" down to dust.
Switched on one heat 12.15 p.m., put retort in 12.30, cut off 5.30.
Room temperature 13 C. Barometer 748 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 3 m.l. and 2 m.l. respectively= 4.0 gall/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.45	377	296	0.4	3.5
3.00	401	329	1.0	5.0
3.15	421	351	3.0	6.8
3.30	433	371	6.8	9.2
3.45	448	388	13.4	12.4
4.00	462	398	21.2	15.0
4.15	475	413	27.2	15.0
4.30	485	430	31.8	13.0
4.45	495	449	34.2	9.2
5.00	504	470	35.8	6.2
5.15	515	487	36.0	2.1
5.35	526	503	36.0	1.0

Water condensed gallons per ton	2.3
Oil yield gallons per ton	36.0
Specific gravity of oil	0.913
Sulphur content of oil	2.15%
Saturation of oil	35%

Distillation analysis of oil not determined

Residue Data

Weight 914 grams Percentage of shale 81.5%

Proximate analysis of residue

Volatiles 5.35% Fixed carbon 2.20% Ash 92.45% Sulphur 1.51%

Sulphur distribution in products of distillation

Residue	40.0%
Oil	10.2
Hydrogen sulphide	34.8
Other gases and loss	±15.0
	100.0

The last item is computed from the Mines Dept. assay of the shale It is possible that this item is somewhat too large.

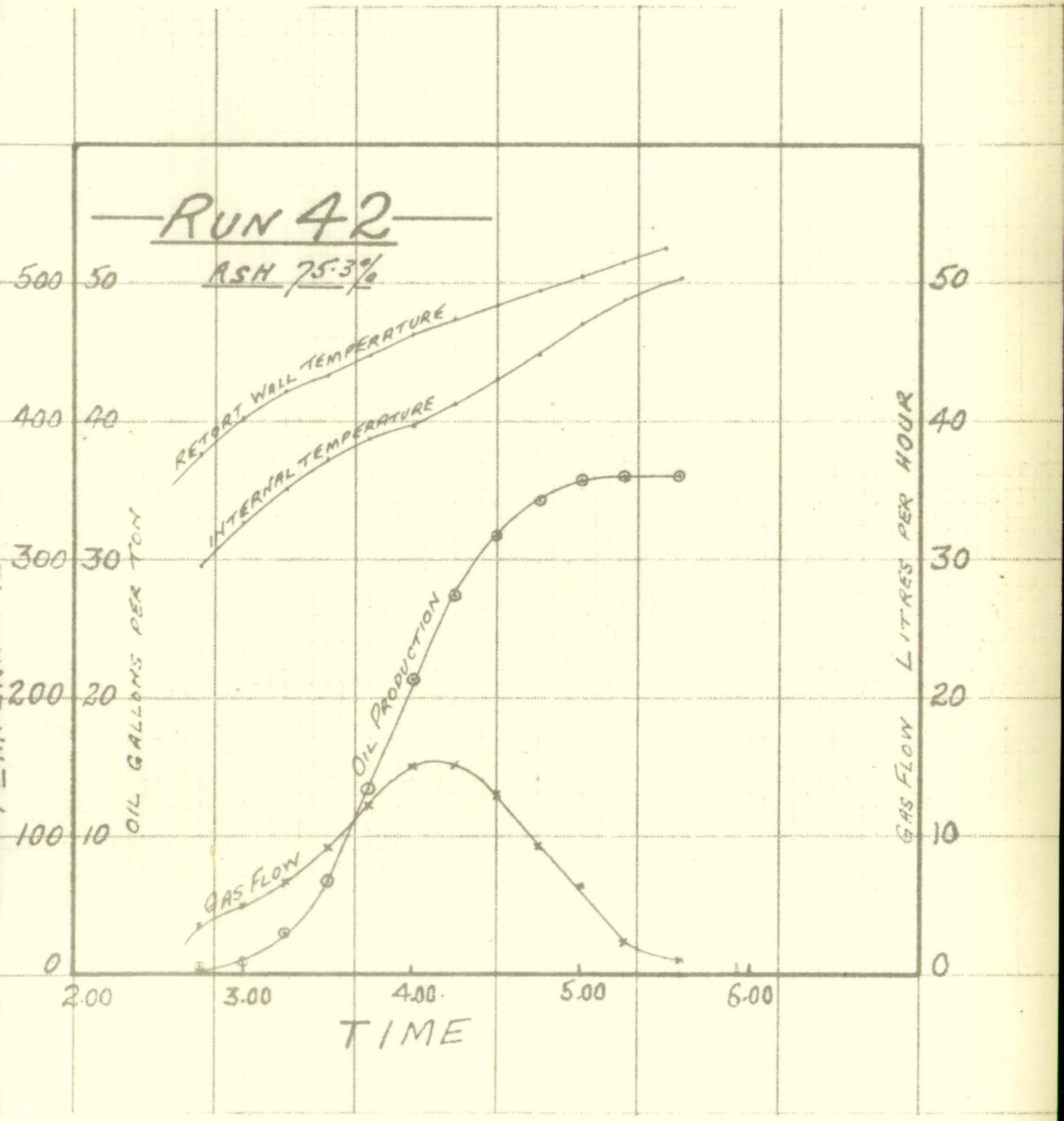
Run No. 42 continued

General Data

Ash/shale ratio		0.753	
Kerogen percentage		24.7%	
Distillation Index		1.45	
Rate of heating in distillation range		65	deg.C/hour
Total time of oil production		2.25	hours
Maximum rate of oil production		28	galls/ton/hour
do. per % kerogen		1.14	
Gas production	Carbon dioxide	64	cu.ft./ton N.T.P.
	Hydrogen sulphide	270	do.
	Scrubbed gas	770	do.
	Total gas	1104	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	75.30%	
Volatiles in residue	4.36	17.65%
Fixed carbon in residue	1.80	7.30
Oil	14.66	59.35
Water condensed	1.03	4.15
Carbon dioxide	0.35	1.45
Hydrogen sulphide	1.14	4.60
Other gases and loss	1.36	5.50
	100.00	100.00


RUN 42
ASH 75.3%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00

RUN No. 43

Charge 1120 grams survey sample 14A bottom seam, Goliath Portland Cement Co's mine, older workings near air shaft No. 2A, ash 81.7%.
Rather fine and dusty.
Switched on 12.15 p.m.
Room temperature 13 C. Barometer 752 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 2.5 m.l. & 2 m.l. respectively = 0.9 gall/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.15	70	70		
2.30	420	370	1.6	6.8
2.45	444	398	4.2	9.6
2.55				12.4
3.00	464	422	9.2	14.0
3.15	480	443	16.6	14.6
3.30	496	466	20.0	12.4
3.45	513	490	22.2	8.0
4.00	527	509	22.6	3.6
4.15	540	527	22.8	2.1
4.30	550	536	22.8	1.5

Water condensed gallons per ton	2.6
Oil yield gallons per ton	22.8
Specific gravity of oil	0.914
Sulphur content of oil	2.28%
Saturation of oil	37%

Distillation analysis of oil not determined

Residue Data

Weight 981 grams Percentage of shale 87.6%

Proximate analysis of residue

Volatiles 6.3% Fixed carbon 0.4% Ash 93.3% Sulphur 1.85%

Sulphur distribution in products of distillation

Residue	57.0%
Oil	7.5
Hydrogen sulphide	23.4
Other gases and loss	12.1%
	100.0

Sulphur content of shale 2.84% Mines Dept. assay

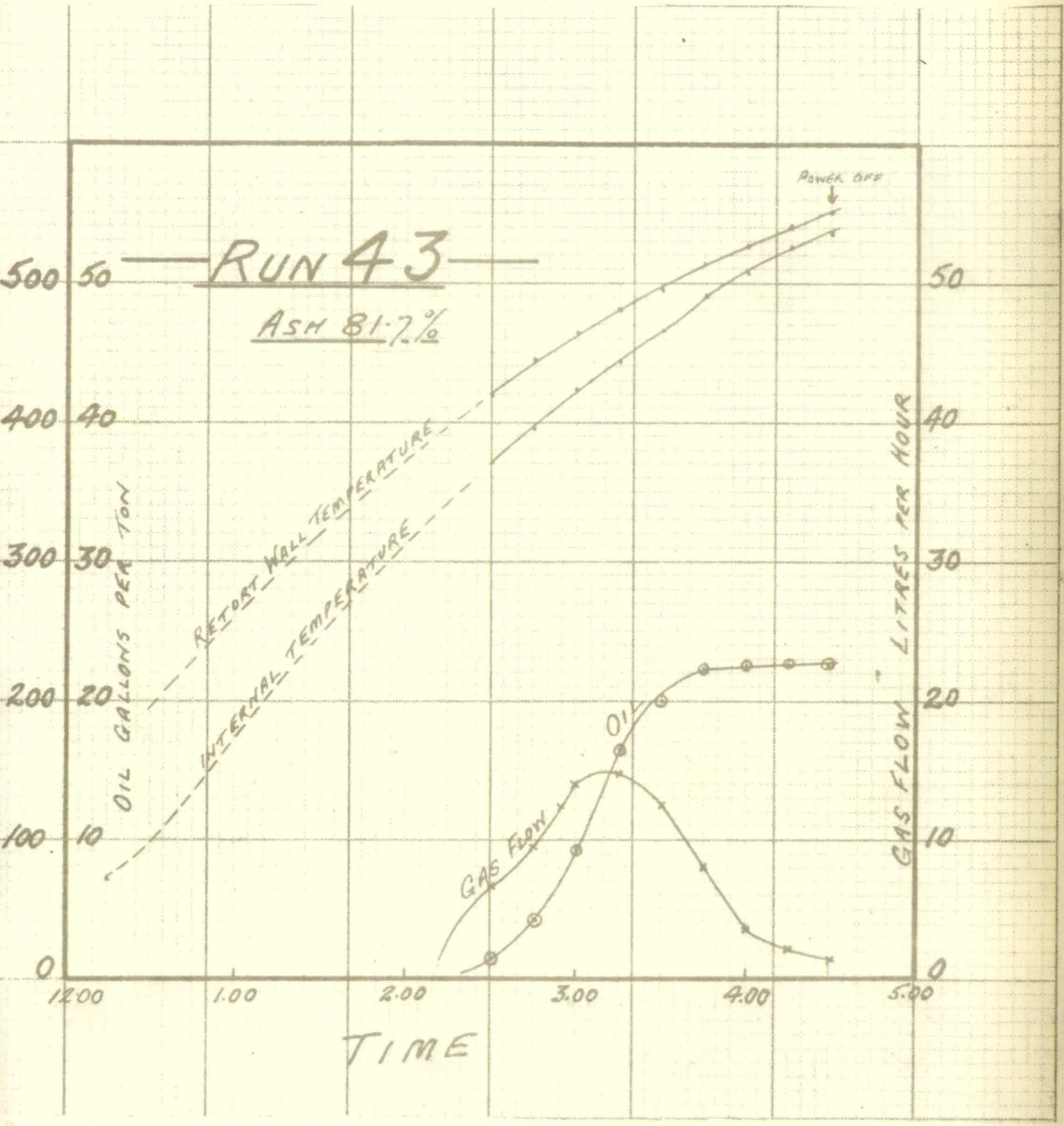
Run No. 43 continued

General Data

Ash/shale ratio		0.817	
Kerogen percentage		18.3	
Distillation Index		1.25	
Rate of heating in distillation range		95	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		30	galls/ton/hour
do. per % kerogen		1.64	do.
Gas production	Carbon dioxide	56	cu.ft./ton N.T.P.
	Hydrogen sulphide	167	do.
	Scrubbed gas	559	do.
	Total gas	782	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	81.70%	
Volatiles in residue	5.52	30.10
Fixed carbon in residue	0.35	1.90
Oil	9.30	50.80
Water condensed	1.16	6.35
Carbon dioxide	0.31	1.70
Hydrogen sulphide	0.71	3.95
Other gases and loss	0.95	5.20
	100.00	100.00


RUN 43
ASH 81·7%
POWER OFF
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
OIL
GAS FLOW
500
400
300
200
100
0
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00
5.00
TIME

RUN No. 44

Charge 1120 grams survey sample 18A, bottom seam from older workings Goliath Portland Cement Co's mine, ash 77.5%.
Rather finely crushed. Room temperature 13 C. Barometer 752 m.m.
Switched on 11.55 a.m., cut off 4.15 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 and 3 m.l. respectively = 1.2 gallons/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.52	166	70		
2.15	398	308	0.8	3.5
2.24				6.2
2.30	424	345	2.0	7.3
2.45	447	374	5.6	12.5
3.00	468	398	12.4	16.0
3.15	490	420	19.6	17.6
3.30	505	442	25.2	15.6
3.45	522	475	28.4	12.5
4.00	536	501	29.6	9.1
4.15	550	518	30.0	4.3
4.30	528	532	30.0	1.5

Water condensed gallons per ton	3.0
Oil yield gallons per ton	30.0
Specific gravity of oil	0.916
Sulphur content of oil	2.12%
Saturation of oil	30%

Distillation analysis of oil not determined

Residue data

Weight 941 grams Percentage of shale 84.0%

Proximate analysis

Volatiles 6.55% Fixed carbon 1.05% Ash 92.4% Sulphur 1.66%

Sulphur distribution in products of distillation

Residue	52.3%
Oil	9.8
Hydrogen sulphide	28.9
Other gases and loss	9.0
	100.0

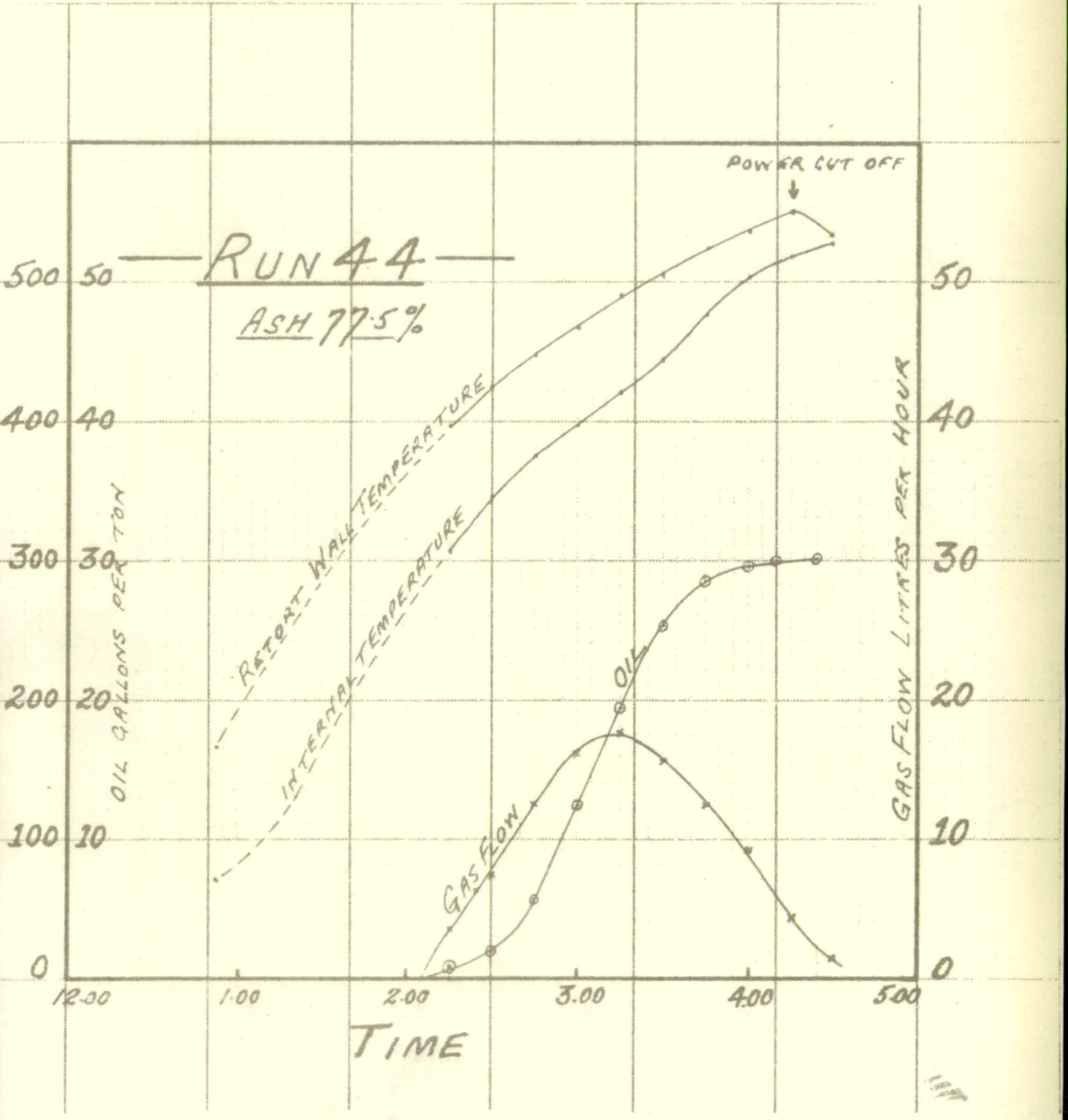
Run No. 44 continued

General Data

Ash/shale ratio		0.775	
Kerogen percentage		22.5%	
Distillation Index		1.33	
Rate of heating in distillation range		100	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		29	galls/ton/hour
do. per % kerogen		1.28	do.
Gas production	Carbon dioxide	54	cu.ft./ton N.T.P.
	Hydrogen sulphide	193	do.
	Scrubbed gas	752	do.
	Total gas	999	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	77.50%	
Volatiles in residue	5.51	24.50%
Fixed carbon in residue	0.88	3.95
Oil	12.26	54.50
Water condensed	1.34	5.95
Carbon dioxide	0.30	1.30
Hydrogen sulphide	0.81	3.60
Other gases and loss	1.40	6.20
	100.00	100.00


RUN 44
ASH 77·5%
POWER CUT OFF
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL
GAS FLOW
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
500
400
300
200
100
0
50
40
30
20
10
0
12·00
1·00
2·00
3·00
4·00
5·00
TIME

RUN No. 45

Charge 1680 grams survey sample 10B, middle band taken from near south fault, Goliath Portland Cement Co's mine, older workings, ash 89.3%, and rather finely crushed.
Switched on 9.00 a.m., cut off 2.00 p.m.
Room temperature 14 C. Barometer 761 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 2 and 1.5 m.l. respectively = 0.5 gall/ton.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
9.30	60	23		
10.00	165	72		
10.30	258	153		
10.45	295	197		
11.02	336	249		
11.15	363	288	0.3	
11.30	394	327	0.4	1.5
11.46	422	361	0.5	6.8
12.00	444	386	1.5	8.5
12.15	466	410	4.4	10.8
12.30	480	427	7.2	9.8
12.45	496	454	8.6	6.2
2.00			9.6	- -

Water condensed gallons per ton	2.3
Oil yield gallons per ton	9.6
Specific gravity of oil	0.908
Sulphur content of oil	2.24
Saturation of oil	35%

Distillation analysis of oil not determined

Residue data

Weight 1574 grams Percentage of shale 93.7%

Proximate analysis of residue

Volatiles 5.1% Fixed carbon -0.4% Ash 95.3% Sulphur 1.46%

RUN No. 45 continued

Sulphur distribution in products of distillation

Residue	69.0%
Oil	4.3
Hydrogen sulphide	28.3
Total recovery	101.6%

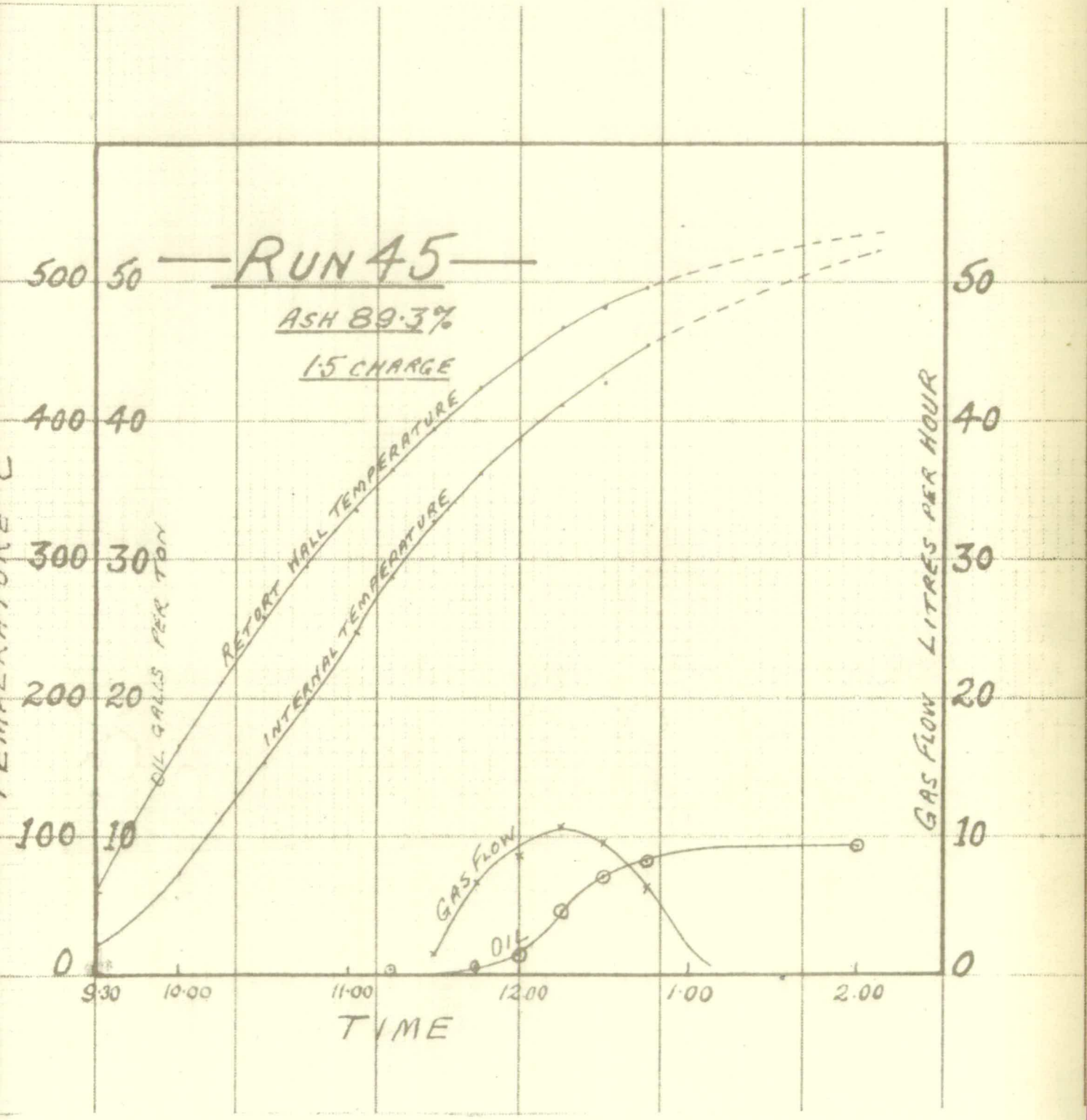
The shale charged contained 1.98% sulphur and the assays were all rechecked without discovering the cause of the over-recovery. As in other cases a pyrites nodule may explain it.

General Data

Ash/shale ratio		0.893	
Kerogen percentage		10.7%	
Distillation Index		0.90	
Rate of heating in distillation range		95	deg.C/hour
Maximum rate of oil production		16	galls/ton/hour
do. per % kerogen		1.50	do.
Total time of oil production		1.5	hours
Gas production	Carbon dioxide	51	cu.ft./ton N.T.P.
	Hydrogen sulphide	155	do.
	Scrubbed gas estimated	226	do.
	Total gas	432	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	89.30%	
Volatiles in residue		
Fixed carbon in residue	4.40	41.10
Oil	3.89	36.40
Water condensed	1.03	9.60
Carbon dioxide	0.28	2.65
Hydrogen sulphide	0.66	6.15
Other gases and loss	0.44	4.10
	100.00	100.00


RUN 45
ASH 89·3%
1·5 CHARGE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL
OIL GALLS PER TON
GAS FLOW LITRES PER HOUR
TEMPERATURE C
TIME
500
400
300
200
100
0
50
40
30
20
10
0
9·30
10·00
11·00
12·00
1·00
2·00

RUN No. 46

Charge 1680 grams survey sample 20B, middle band, taken from Goliath Portland Cement Co's mine, older workings, ash 89.8%, in size from ½" down.
Switched on 5.00 p.m. Cut off 8.30 p.m.
Room temperature 14 C. Barometer 761 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 1.5 and 1.5 m.l. respectively = 0.4 gall/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
5.45	199	105		
7.00	408	330	0.4	1.5
7.15	438	370	1.1	6.8
7.30	461	398	3.5	10.0
7.45	483	422	5.3	10.0
8.00	503	445	6.8	6.2
8.15	526	479	7.3	3.0
8.30	539	500	7.5	1.5

Water condensed gallons per ton	2.8
Oil yield gallons per ton	7.5
Specific gravity of oil	0.910
Sulphur content of oil	2.36%
Saturation of oil	31%

Distillation analysis of oil not determined

Residue Data

Weight 1589 grams Percentage of shale 94.5%

Proximate analysis of residue

Volatiles 6.45% Fixed carbon -1.45% Ash 95.0% Sulphur 3.15%

It will be noticed that the fixed carbon is negative. This is due partly to the low actual fixed carbon in the resdiue from the poor shales and partly to the gain in weight by oxidation of sulphur and possibly arsenic and retention in the residue. The latter effect is sometimes greater than the actual loss of carbon by oxidation, giving a negative fixed carbon result as is decidedly the case in this analysis. The sulphur content of this shale was 3.57% of which the greater part would be as pyrites.

Run No. 46 continued

Sulphur distribution in products of distillation

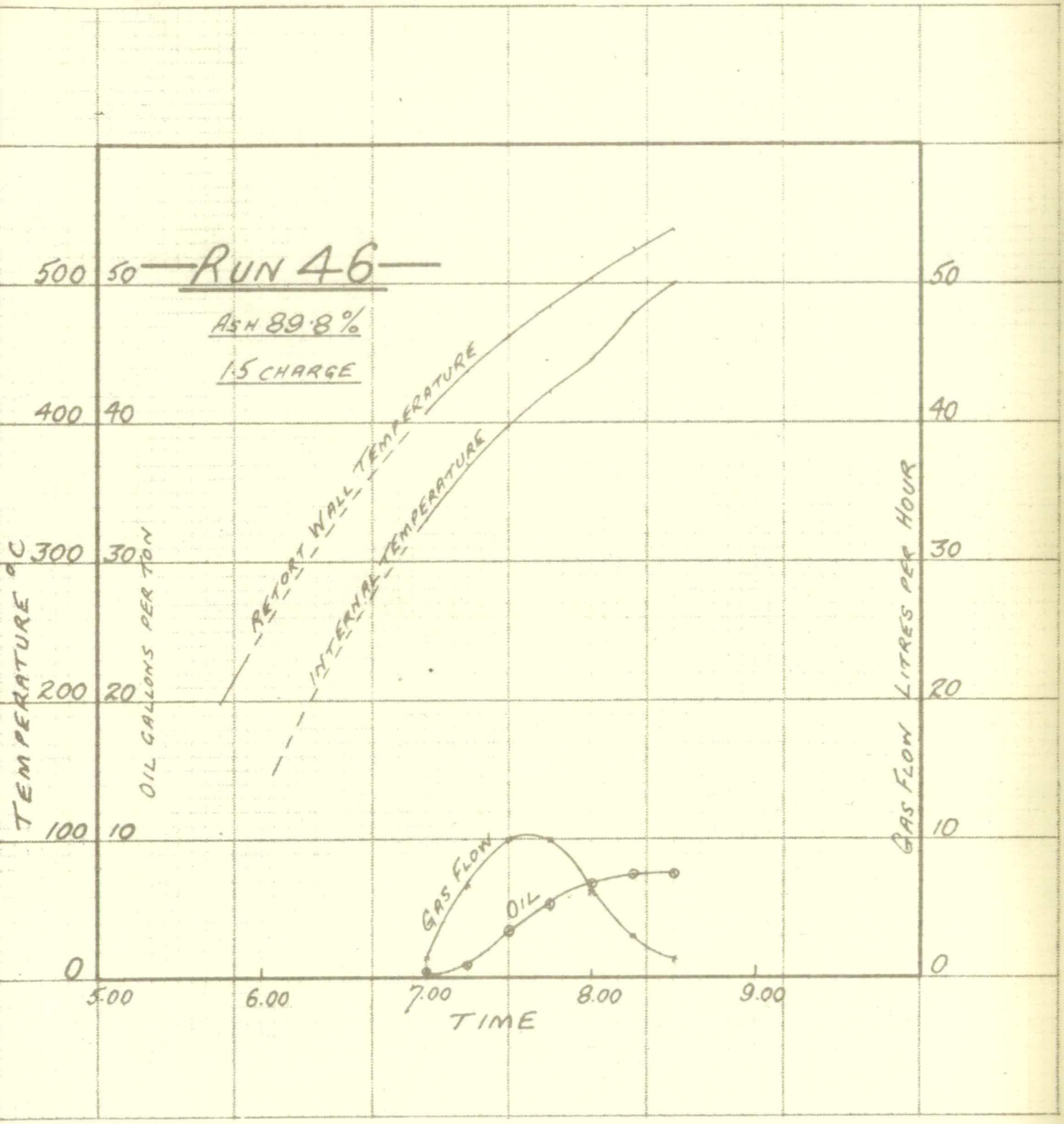
Residue	83.5%
Oil	2.0
Hydrogen sulphide	12.9
Other gases and loss	1.6
	100.0

General Data

Ash/shale ratio		0.898	
Kerogen percentage		10.2	
Distillation Index		0.73	
Rate of heating in distillation range		105	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		10	galls/ton/hour
do. per % kerogen		0.98	do.
Gas production	Carbon dioxide	41	cu.ft./ton N.T.P.
	Hydrogen sulphide	116	do.
	Scrubbed gas	195	do.
	Total gas	352	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	89.80%	
Volatiles in residue		
Fixed carbon in residue together	4.72	46.35%
Oil	3.04	29.95
Water condensed	1.25	12.25
Carbon dioxide	0.23	2.05
Hydrogen sulphide	0.49	4.80
Other gases and loss	0.47	4.60
	100.00	100.00


RUN 46
ASH 89·8%
1·5 CHARGE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
500
400
300
200
100
0
50
40
30
20
10
0
5.00
6.00
7.00
8.00
9.00
TIME
GAS FLOW
OIL

RUN No. 47

Charge 1120 grams survey sample 6C, top seam, from Goliath Portland Cement Co's mine, New Tunnel, crushed through ½" screen, ash 71.6%, sulphur content 2.28%.
Switched on 12.00 noon, cut off 4.30 p.m.
Room temperature 14 C. Barometer 759 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Oil scrubber catches 2.5 and 3.0 m.l. respectively= 1.1 gall/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.30	95	25		
2.05	398	293	1.6	5.0
2.22	426	331	2.0	7.5
2.30	439	351	3.8	10.4
2.45	459	374	12.6	16.0
3.00	481	400	25.8	19.3
3.15	503	422	36.0	18.4
3.30	522	445	43.2	15.5
3.48	541	495	45.8	8.0
4.00	556	518	46.0	3.5
4.17	573	541	46.2	3.0

Water condensed gallons per ton	2.4
Oil yield gallons per ton	46.2
Specific gravity of oil	0.913
Sulphur content of oil	2.36
Saturation of oil	30%

Distillation analysis of oil not determined

Residue Data

Weight 863 grams Percentage of shale 77.0%

Proximate analysis of residue

Volatiles 4.55% Fixed carbon 2.4% Ash 93.05% Sulphur 1.25%

Sulphur distribution in products of distillation

Residue	42.2%
Oil	19.5
Hydrogen sulphide	37.8
Other gases and loss	± 0.5
	100.0

It is possible that the third item should be 34.4 and the fourth 3.9 as later work showed a pipette to be 10% too large. It is not certain, however, that the inaccurate pipette was used.

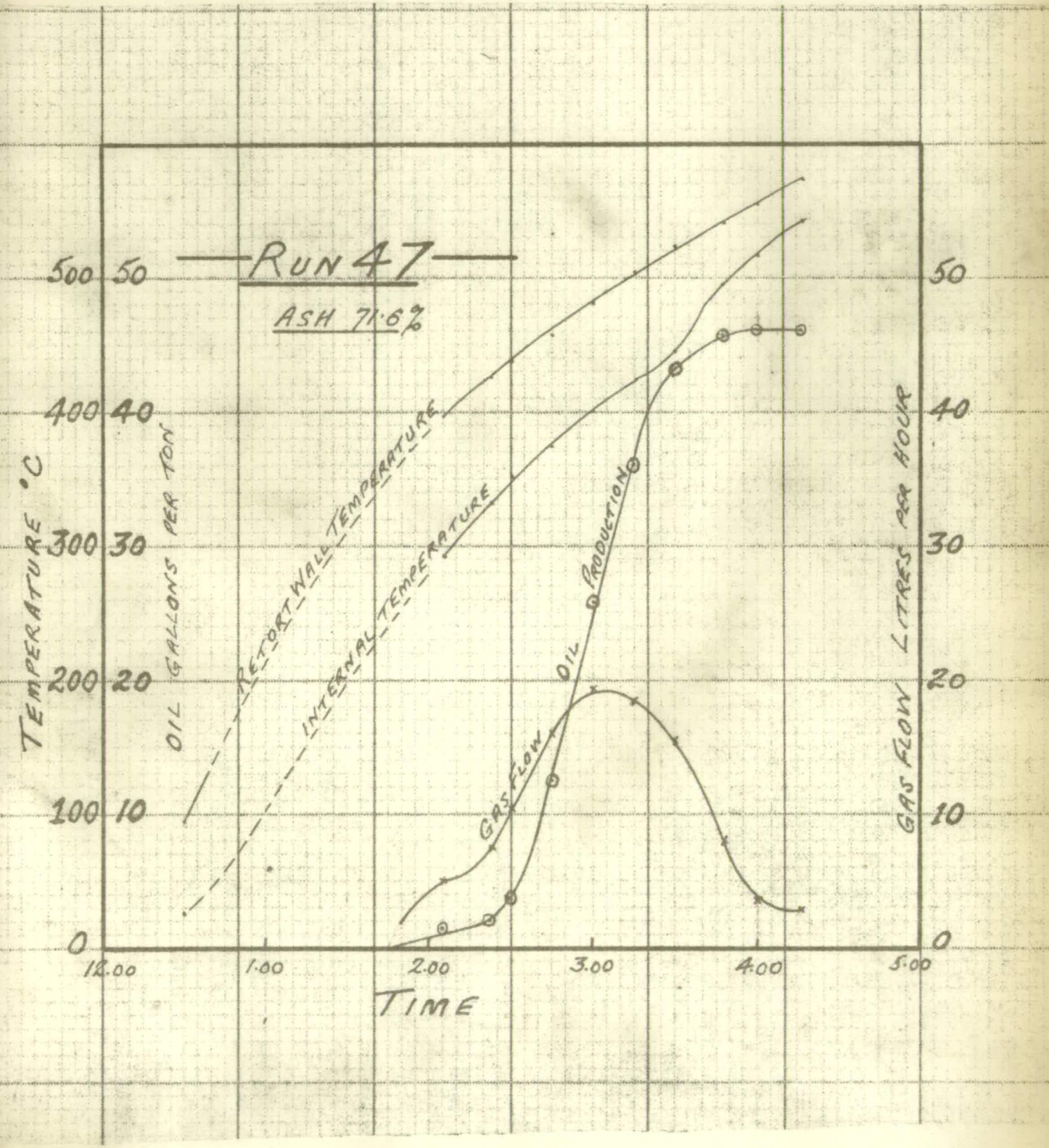
Run No. 47 continued

General Data

Ash/shale ratio		0.716	
Kerogen percentage		28.4	
Distillation Index		1.62	
Rate of heating in distillation range		105	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		48	galls/ton/hour
do. per % kerogen		1.69	do.
Gas production	Carbon dioxide	64	cu.ft./ton N.T.P.
	Hydrogen sulphide	216	do.
	Scrubbed gas	775	do.
	Total gas	1055	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	71.60%	
Volatiles in residue	3.50	12.30%
Fixed carbon in residue	1.85	6.50
Oil	18.82	66.28
Water condensed	1.07	3.77
Carbon dioxide	0.35	1.24
Hydrogen sulphide	0.91	3.22
Other gases and loss	1.90	6.69
	100.00	100.00


RUN 47
ASH 71·6%
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
500
400
300
200
100
0
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00
5.00
TIME

RUN No. 48

Charge 1120 grams survey sample 190, top seam, taken from near the centre of the older workings, Goliath Portland Cement Co's mine, ash 80.2%, sulphur content 2.06%, crushed through ½" screen.
Switched on 12.10 p.m., cut off 4.15 p.m.
Room temperature 15 C. Barometer 757 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 2.5 & 3.0 m.l. = 1.1 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.50	105	35		
2.30	411	342	0.8	6.8
2.47	440	377	4.2	11.0
3.00	462	405	9.6	15.0
3.15	480	427	18.4	16.0
3.30	501	454	24.4	13.5
3.45	518	483	27.2	8.5
4.00	536	509	27.6	3.5
4.15	551	531	27.6	2.2
4.30	537	537	27.6	1.0

Water condensed gallons per ton	3.0
Oil yield gallons per ton	27.6
Specific gravity of oil	0.912
Sulphur content of oil	2.18%
Saturation of oil	31%
Distillation analysis of oil not determined	

Residue Data

Weight 961 grams Percentage of shale 85.9%

Proximate analysis of residue

Volatiles 5.75% Fixed carbon 0.75% Ash 93.5% Sulphur 1.35%

Sulphur distribution in products of distillation

Residue	55.1%
Oil	11.8
Hydrogen sulphide	29.5
Other gases and loss	3.6
	100.0

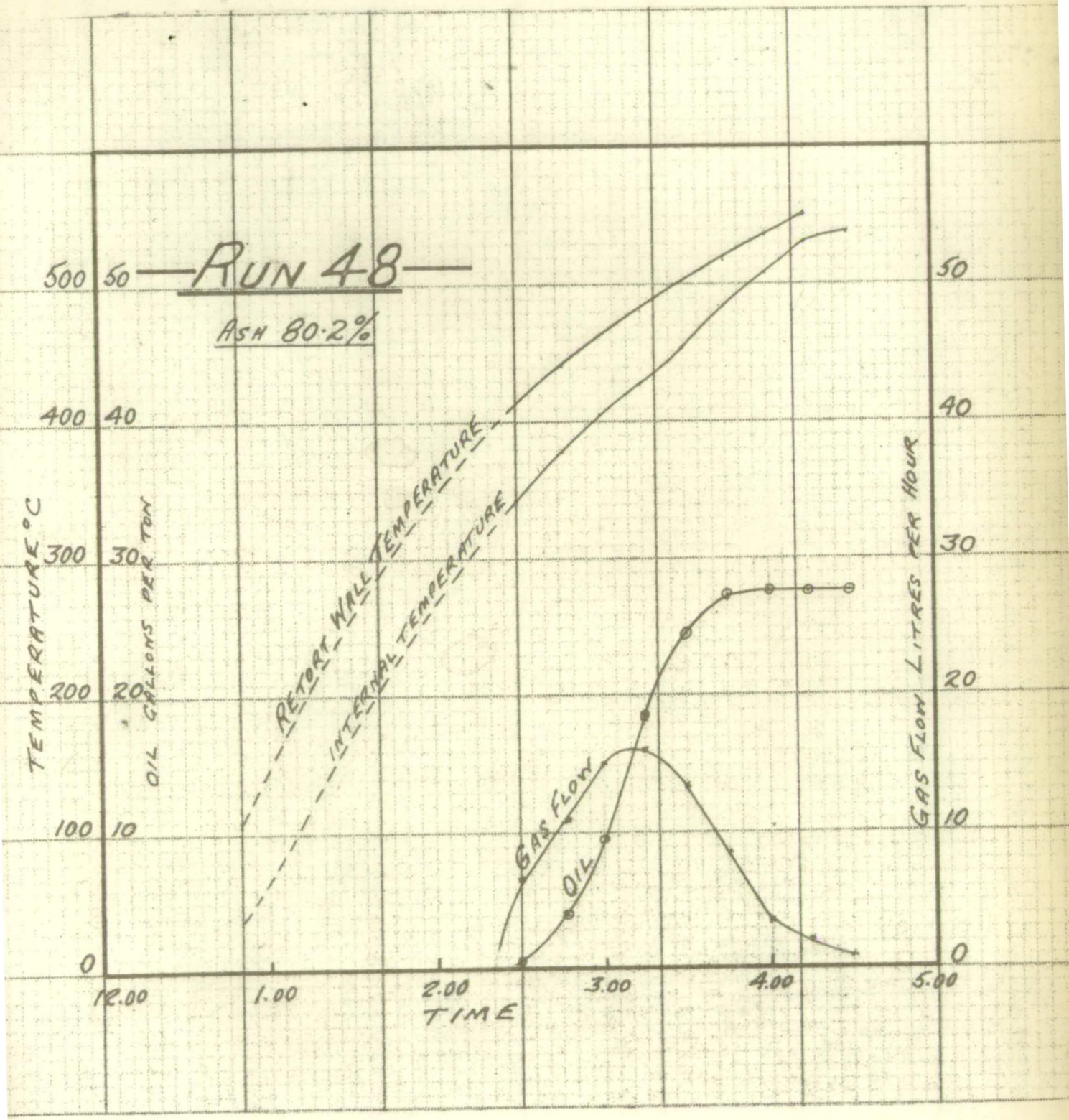
Run No. 48 continued

General Data

Ash/shale ratio		0.802	
Kerogen percentage		19.8	
Distillation Index		1.39	
Rate of heating in distillation range		110	deg.C/hour
Total time of oil production		1.5	hours
Maximum rate of oil production		38	galls/ton/hour
do. per% kerogen		1.92	do.
Gas production	Carbon dioxide	39	cu.ft./ton N.T.P.
	Hydrogen sulphide	153	do.
	Scrubbed gas	519	do.
	Total gas	711	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	80.20%	
Volatiles in residue	4.94	24.90%
Fixed carbon in residue	0.64	3.25
Oil	11.23	56.75
Water condensed	1.34	6.75
Carbon dioxide	0.22	1.10
Hydrogen sulphide	0.65	3.30
Other gases and loss	0.78	3.95
	100.00	100.00


RUN 48
ASH 80·2%
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL
TIME
500
400
300
200
100
0
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00
5.00

RUN No. 42

Charge 1120 grams standard sample 66.6% ash, in ¼" thickness flakes. Distilled at a rate of heating of 100 C/hour under an absolute pressure varying from 1.5 to 2.5 pounds per square inch.
Switched on 12.30 p.m., cut off 5.30 p.m.
Room temperature 15 C. Barometer 750 m.m.
Gas scrubbed to remove hydrogen sulphide and exhausted to waste.
Oil scrubber catches 2 and1 m.l. respectively = 0.6 gallon/ton.
Scrubbing was performed at an average pressure of approx. one seventh atmosphere so that the scrubber spirit recovery is only a fraction of what may have been recovered had the gasses been raised to atmospheric pressure before scrubbing. No suitable pump was available for this purpose.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	ABSOLUTE PRESS CM. OF MERCURY
2.30	370	318	0.4	
2.45	400	361	2.4	15
3.00	433	396	7.0	11
3.15	455	416	18.6	12
3.30	472	433	30.0	12
3.45	492	468	37.8	10
4.00	515	502	41.8	9
4.15	531	523	45.2	7
4.30	550	539	48.4	7
4.50	568	561	49.4	7
5.00	575	573	50.2	7
5.30	598	599	50.6	7

Water condensed gallons per ton	5.8
Oil yield gallons per ton	50.6 actual recovery
Specific gravity of oil	0.946
Sulphur content of oil	2.36%
Saturation of oil	16%

Residue Data

Weight 805 grams Percentage of shale 71.8%

Proximate analysis of residue

Volatiles 3.9% Fixed carbon 3.25% Ash 92.85% Sulphur 2.09%

Run No. 49 continued

Sulphur distribution in products of distillation

Residue	57.7%
Oil	19.5
Hydrogen sulphide	19.5
Other gases and loss	3.3
	100.0

General Data

Ash/shale ratio		0.666	
Kerogen percentage		33.4%	
Distillation Index (on actual oil yield)		1.52	
Rate of heating in distillation range		100	deg.C/hour
Total time of oil production		2.5	hours
Maximum rate of oil production		46	galls/ton/hour
do. per % kerogen		1.38	do.
Gas production	Carbon dioxide	62	cu.ft.ton N.T.P.
	Hydrogen sulphide	127	do.

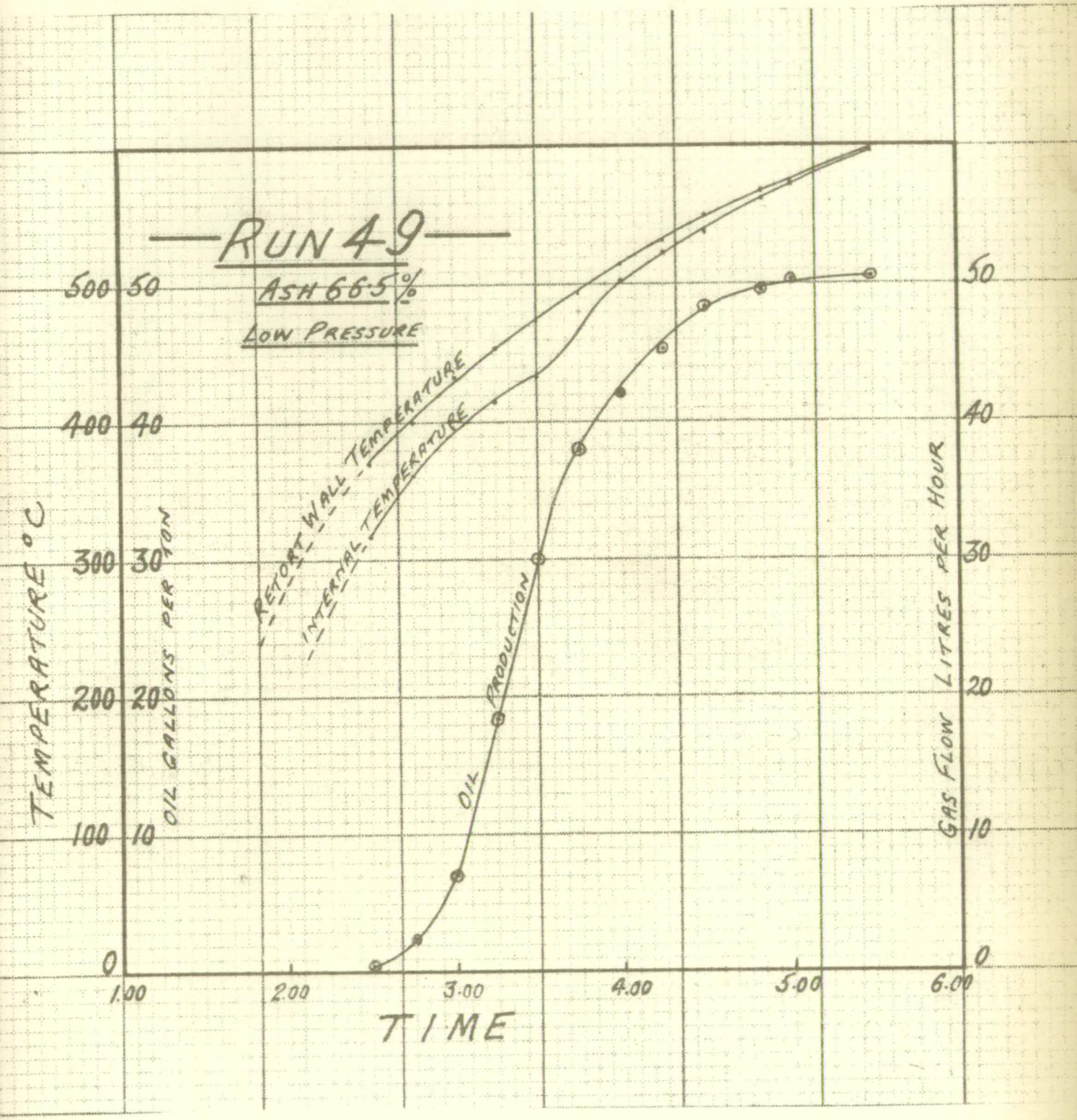
Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.60%	
Volatiles in residue	2.80	8.40%
Fixed carbon in residue	2.34	7.00
Oil	21.36	64.00
Water condensed	2.58	7.75
Carbon dioxide	0.34	1.00
Hydrogen sulphide	0.54	1.60
Other gases and loss	3.44	10.25
	100.00	100.00

Note.

The last item is higher than usual from two distinct causes. The poor spirit scrubbing has made part of the oil yield appear as gases and in addition to this the distillation was carried to 600 C which would have the effect of expelling some of the volatiles usually left in the shale residue.

The retort was a little out of position with the result that one end was cool. This explains the the slow tailing off the oil production.


RUN 49
ASH 66·5%
LOW PRESSURE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 50

Charge 1120 grams survey sample 190, as used in Run 48, ash 79.7% sulphur content 2.06%, crushed through ½" screen.
Distilled at a rate of heating of 100 C per hour under an absolute pressure of 1.5 to 2.0 pounds per square inch.
Switched on 12.30 p.m., cut off 5.00 p.m.
Room temperature 15 C. Barometer 753 m.m.
Gas scrubbed to remove hydrogen sulphide and exhausted to waste.
Oil scrubber catches 2 and3 m.l. = 1.0 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	RETORT PRESS. CM. MERCURY
2.21	363	267	0.4	
2.30	381	292	1.0?	7
2.45	410	326	1.2?	7.5
3.00	435	358	2.8	9.0
3.15	459	386	8.2	10.0
3.30	480	410	15.8	10
3.45	498	432	22.4	9
4.00	515	457	27.0	8
4.15	528	481	28.4	7.5
4.30	542	503	28.8	7.5
5.00	564	541	29.0	

Water condensed gallons per ton	2.2
Oil yield gallons per ton	29.0
Specific gravity of oil	0.945
Sulphur content of oil	2.14%
Saturation of oil	18%

Distillation analysis of oil not determined

Residue Data

Weight 948 grams Percentage of shale 84.6%

Proximate analysis of residue

Volatiles 5.7% Fixed carbon 0.2% Ash 94.1% Sulphur 1.49%

Sulphur distribution in products of distillation

Residue	61.2%
Oil	12.6
Hydrogen sulphide	22.2
Other gases and loss	4.0
	100.0

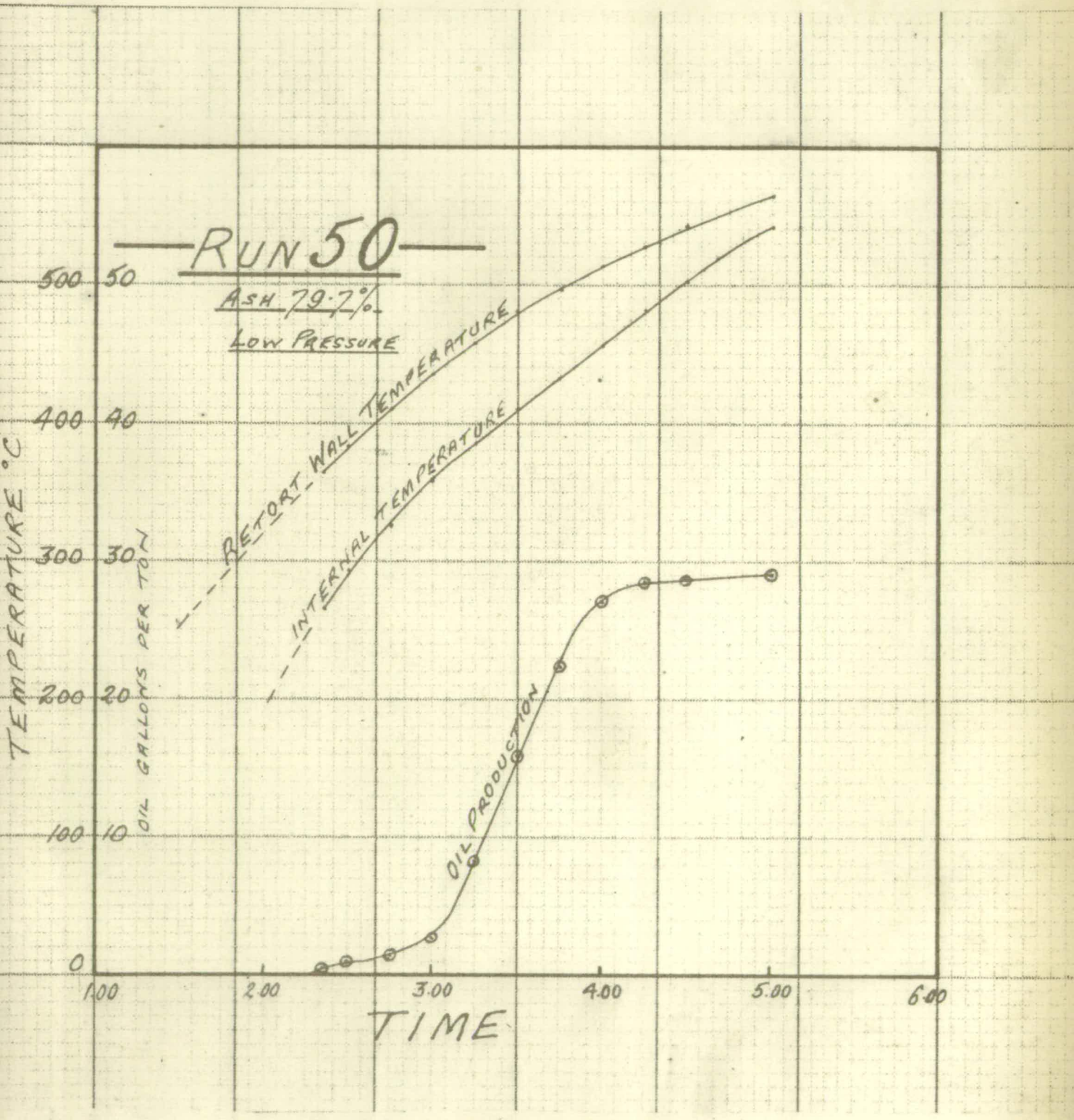
Run No. 50 continued

General Data

Ash/shale ratio		0.797	
Kerogen percentage		20.3	
Distillation Index		1.43	
Rate of heating in distillation range		100	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		28	galls/ton/hour
do. per % kerogen		1.38	do.
Gas production	Carbon dioxide	16	cu.ft./ton N.T.P.
	Hydrogen sulphide	115	do.

Weight Balance on productd of distillation

	Percentage of shale	On ashless basis
Ash	79.70%	
Volatiles in residue	4.82	23.70%
Fixed carbon in residue	0.17	0.85
Oil	12.23	60.30
Water condensed	0.98	4.80
Carbon dioxide	0.09	0.45
Hydrogen sulphide	0.48	2.35
Other gases and loss	1.53	7.55
	100.00	100.00


RUN 50
ASH 79·7%
LOW PRESSURE
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
TEMPERATURE °C
OIL GALLONS PER TON
500
400
300
200
100
0
50
40
30
20
10
1.00
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 51

Charge 1120 grams of shale from Crozier retort feed, end of March 1932, ash 71.3%, in ¼" flakes.
Distilled at a rate of heating of 100 C per hour.
Switched on 12.10 p.m., cut off 4.35 p.m.
Room temperature 16 C. Barometer 759 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 & 4 m.l. respectively = 1.4 galls/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.45	112	35		
1.05	184	83		
1.30	266	150		
1.45	307	200		
2.00	344	241	0.2	0.3
2.15	376	284	0.6	2.0
2.20				3.5
2.25				4.0
2.30	407	322	1.8	4.5
2.35				4.5
2.40				6.8
2.45	433	358	4.6	9.2
2.50				11.7
2.55				13.3
3.00	454	381	11.2	15.3
3.05				17.4
3.10				19.0
3.15	474	403	23.2	20.0
3.20				21.2
3.25				21.8
3.30	496	423	35.8	21.2
3.35				20.6
3.40				19.3
3.45	513	442	43.3	17.4
3.50				14.3
3.55				11.7
4.00	531	484	45.7	9.0
4.05				6.3
4.10				4.5
4.15	547	515	45.9	4.0
4.20				3.5
4.31	564	536	45.9	3.0
4.45	556	549	45.9	0.5

Water condensed gallons per ton	2.6
Oil yield gallons per ton	45.9
Specific gravity of oil	0.913
Sulphur content of oil	2.46%
Saturation of oil	30%

Residue Data

Weight 865 grams Percentage of shale 77.2%

Proximate analysis of residue

Volatiles 4.6% Fixed carbon 3.0% Ash 92.4% Sulphur 1.48%

Sulphur distribution in products of distillation

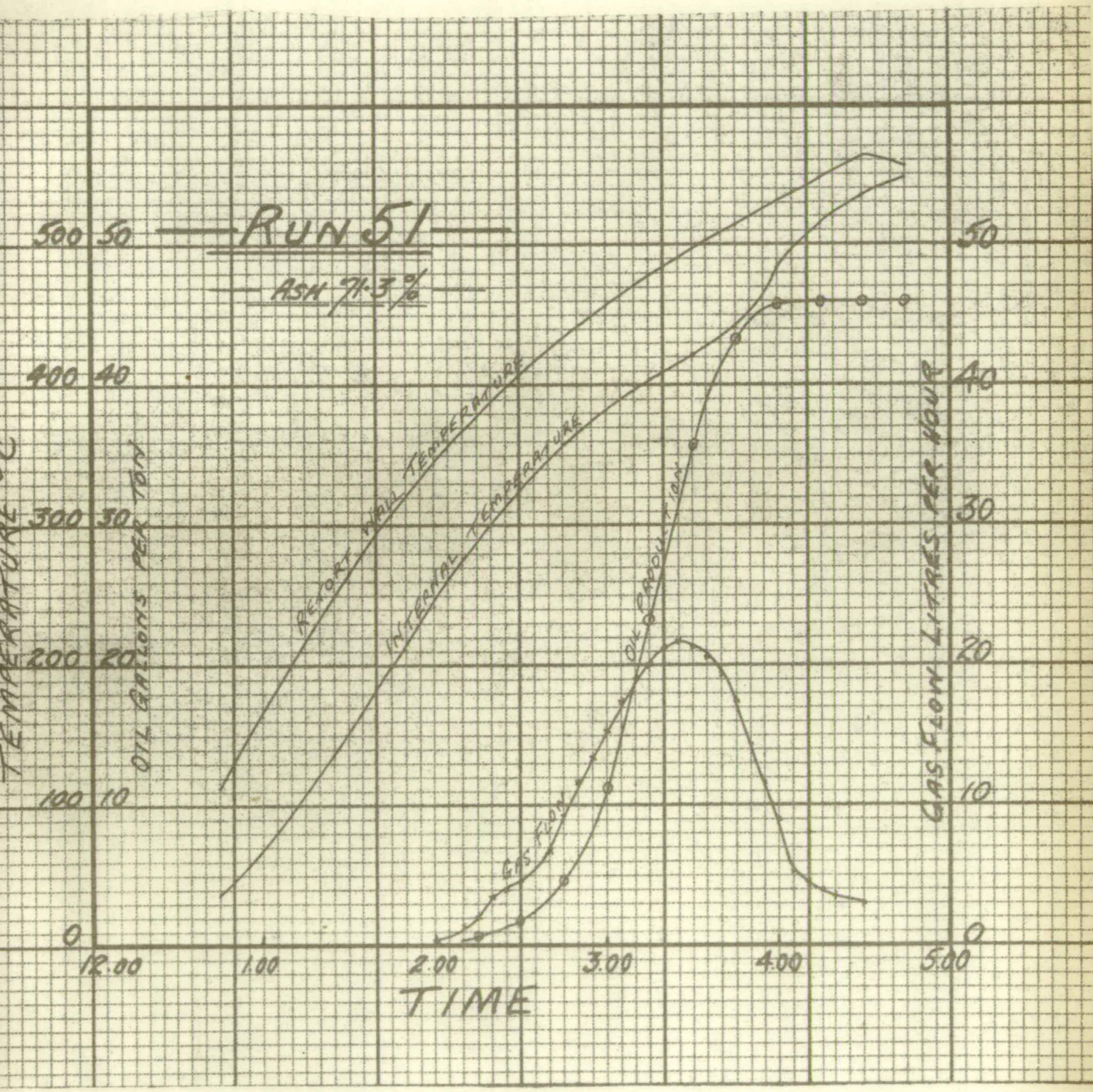
Residue 12.8 grams, Oil 5.16 grams, Hydrogen sulphide 13.16 grams.
Total recovery 31.09 grams = 2.78% of shale.

General Data

Ash/shale ratio		0.713	
Kerogen percentage		28.7%	
Distillation Index		1.60	
Rate of heating in distillation range		100	deg.C/hour
Total time of oil production		1.75	hours
Maximum rate of oil production		50	galls/ton/hour
do. per % kerogen		1.74	do.
Gas production	Carbon dioxide	39	cu.ft./ton N.T.P.
	Hydrogen sulphide	294	do.
	Scrubbed gas	812	do.
	Total gas	1145	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	71.33%	
Volatiles in residue	3.55	12.30%
Fixed carbon in residue	2.32	8.10
Oil	18.72	65.35
Water condensed	1.16	4.05
Carbon dioxide	0.21	0.75
Hydrogen sulphide	1.25	4.35
Other gases and loss	1.46	5.10
	100.00	100.00


RUN 51
ASH 71.3%
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
REACTOR WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
GAS FLOW
500
400
300
200
100
0
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00
5.00
TIME

RUN No. 52

Charge 1120 grams standard sample dried to constant weight at 100 C, ash 67.1%, in ¼" thickness flakes.
Distilled slowly in steady current of steam generated by electric heater. Steam started 11.00 a.m., stopped 4.50 p.m.
Switched on heating power 9.07 a.m., cut in regulating rheostat at 11.00 a.m., cut off 6.00 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 6 & 5 m.l. = 2.2 gallons per ton.
The progressive figures on oil production could not be obtained owing to the slow separation of oil and water. An approximate value of the maximum rate of oil production was obtained.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	GAS FLOW LITRES/HOUR
10.15	211	111	
10.30	252	151	
10.45	296	201	
11.00	332	247	
11.15	348	288	0.7
11.30	344	314	0.7
11.45	349	322	0.7
12.00	366	333	0.7
12.15	376	344	1.4
12.30	386	355	2.8
12.45	394	365	4.2
1.00	403	373	4.9
1.15	413	382	6.3
1.30	421	390	9.0
1.45	430	398	12.0
2.00	438	407	15.0
2.20	450	416	17.3
2.30	454	422	18.0
2.45	462	430	14.5
3.00	468	438	12.0
3.15	476	449	10.3
3.30	485	460	8.0
3.45	493	467	6.3
4.00	501	477	5.3
4.15	509	486	5.0
4.30	519	496	4.0
4.45	525	505	3.5
5.00	533	511	0.7
5.30	542	526	
6.00	546	533	

Steam used as gallons water per ton	77
Oil yield gallons per ton	50.2
Specific gravity of oil	0.929
Sulphur content of oil	2.34%
Saturation of oil	28%

Run No. 52 continued

Residue Data

Weight 833.5 grams Percentage of shale 74.4%

Proximate analysis of residue

Volatiles 5.75% Fixed carbon 4.0% Ash 90.25% Sulphur 1.88%

Sulphur distribution in products of distillation

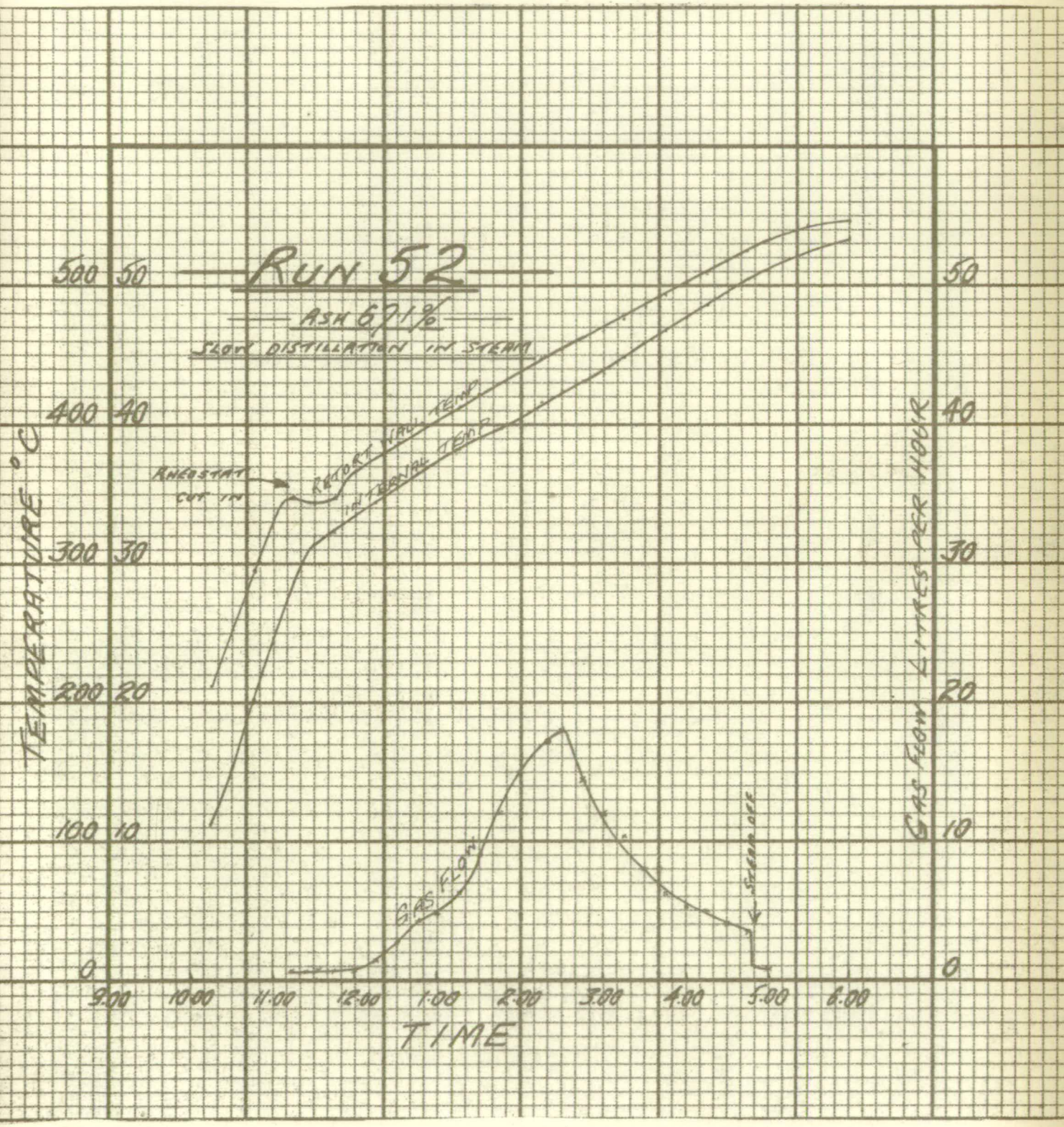
Residue	53.9%
Oil	18.7
Condensed water	0.4
Hydrogen sulphide	24.5
Other gases and loss	2.5
	100.0

General Data

Ash/shale ratio		0.671	
Kerogen percentage		32.9	
Distillation Index		1.52	
Rate of heating in distillation range		35	deg.C/hour
Total time of oil production		5.0	hours
Maximum rate of oil production		20	galls/ton/hour
do per % kerogen		0.61	do.
Gas production	Carbon dioxide	62	cu.ft./ton N.T.P.
	Hydrogen sulphide	163	do.
	Scrubbed gas	1250	do.
	Total gas	1475	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	67.10%	
Volatiles in residue	4.28	13.00%
Fixed carbon in residue	2.98	9.05
Oil	20.80	63.20
Carbon dioxide	0.34	1.05
Hydrogen sulphide	0.69	2.10
Other gases, water produced by shale, and loss.	3.81	11.60
	100.00	100.00


RUN 52
ASH 6.71%
SLOW DISTILLATION IN STEAM
RHEOSTAT CUT IN
RHEOSTAT CUT OUT
IN TEMPERATURE TREND
IN TEMPERATURE TREND
GAS FLOW
STEAM OFF
TEMPERATURE °C
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
9.00
10.00
11.00
12.00
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 52

Charge 1120 grams standard sample ash 67.2% in ¼" thickness flakes. Retorted approximately isothermally by holding the temperature between 400 C and 410 C for about 50 hours and then raising the temperature to the ususal finishing temperature for comparative purposes.
Room temperature average about 15 C. Barometer 773 m.m.
Switched on 9.10 a.m. April 12th. Cut in rheostat 12.20 p.m.
Cut out rheostat 2.30 p.m. April 14th, cut off 5.50 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 & 2 m.l. respectively = 1.0 gallon/ton.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
April 12				
10.00 a.m.	130	57		
10.30	214	124		
11.00	282	199		
11.30	339	272	0.4	0.7
12.00	382	332	2.0	2.0
12.20				6.8
12.30	410	376	5.0	8.4
1.30	401	390	16.6	5.0
2.00	397	385	19.4	3.5
2.30	407	386	21.2	4.2
3.00	414	398	26.4	6.0
3.30	413	401	27.6	4.6
4.00	412	400	29.2	3.5
4.30	410	398	29.8	3.0
5.00	408	398	31.8	2.0
5.30	406	396	33.4	1.4
7.00	406	397	34.0	0.7
7.30	410	398	34.2	0.7
8.00	412	402	35.0	0.7
8.30	411	403	35.2	?
9.00	413	401	35.4	?
9.30	411	402	35.8	?
10.00	410	410	36.0	?
April 13				
9.30 a.m.	402	392	38.2	?
12.00	403	393	38.6	?
2.00 p.m.	410	410	38.8	?
5.00	410	404	39.2	?
April 14				
10.00 a.m.	420	415	40.6	?
12.00	411	405	40.8	?
2.00 p.m.	410	404	40.8	?
3.00	446	428		
3.30	479	462	41.0	?
4.00	506	487	41.2	3.5
5.05	544	523	41.4	2.8
5.30	556	544	41.7	

Run No. 53 continued

Note

This run was intended to be carried out at 400 C and not over 405C. The temperatures as indicated by the thermocouples using an older calibration curve did actually exceed this upper limit owing to the length of the distillation and varying voltage of the College mains due to the varying load over the day. In addition recalibration of the thermocouples after this run showed a difference of 5 degrees Centigrade from the previous calibration at 400 C. This increased the actual temperature figures by 5 degrees making the actual temperature of the distillation perceptibly higher than intended. The figures given on the previous page are the corrected ones. At 400 C the behaviour of the shale would be very similar only a longer distillation would be necessary and for these reasons another distillation was not carried out.

Inspection of the temperature figures will show that the internal temperature is consistently below the wall temperature even when both temperatures are practically stationary for a considerable time. Comparison of the two couples at 400 C showed them to be one degree apart in their indications so that the difference between the two couples must have been due to conduction of heat along the internal tube to the somewhat cooler retort end.

The amount of scrubbed gas is probably on the low side as the flow meter could not be read after 8 p.m. on April 12th.

Water condensed during distillation	6.5	gallons/ton
Oil yield in isothermal stage	40.8	do.
Oil yield on raising temperature to 556 C	0.9	do.
Total oil yield	41.7	do.
Specific gravity of oil	0.898	
Sulphur content of oil	2.37	
Saturation of oil	44%	

The oil produced was very similar to that produced in Run 26 as regards gravity etc. The distillation analysis was not performed as Oil 26 was within 0.001 of Oil 53 in specific gravity and the distillation analysis is given in the record of that run.

Run No. 53 continued

Residue Data

Weight 853.5 grams Percentage of shale 76.2%

Proximate analysis of residue

Volatiles 5.4% Fixed carbon 6.4% Ash 88.2% Sulphur 2.06%

Sulphur distribution in products of distillation

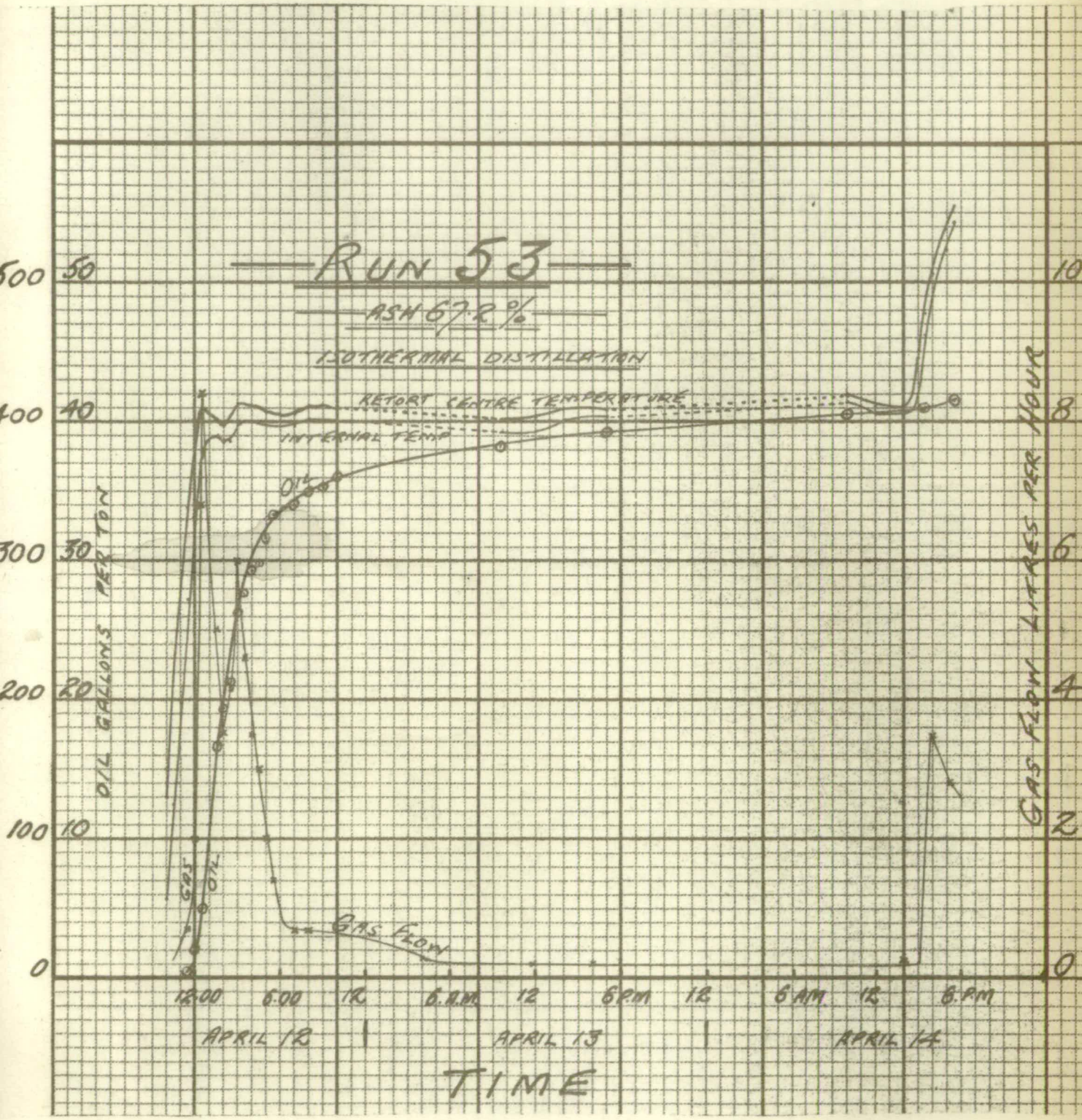
Residue	60.4%
Oil	15.2
Hydrogen sulphide	18.8
Other gases and loss	5.6
	100.0

General Data

Ash/shale ratio		0.672	
Kerogen percentage		32.8	
Distillation Index		1.27	
Rate of heating in distillation range			approx. isothermal
Total time of oil production		54	hours
Maximum rate of oil production		11.6	galls/ton/hour
do. per % kerogen		0.35	do.
Gas production	Carbon dioxide	56	cu.ft./ton N.T.P.
	Hydrogen sulphide	123	do.
	Scrubbed gas	845?	do.
	Total gas	1024	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	67.20%	
Volatiles in residue	4.12	12.55%
Fixed carbon in residue	4.88	14.90
Oil	16.66	50.75
Water condensed	2.90	8.85
Carbon dioxide	0.31	0.95
Hydrogen sulphide	0.52	1.60
Other gases and loss	3.41	10.40
	100.00	100.00


RUN 53
ASH 67.2 %
ISOTHERMAL DISTILLATION
RETORT CENTRE TEMPERATURE
INTERNAL TEMP
OIL
GAS
OIL
GAS FLOW
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
500
400
300
200
100
0
50
40
30
20
10
0
10
8
6
4
2
0
12.00
6.00
12
6 A.M.
12
6 P.M.
12
6 A.M.
12
6 P.M.
APRIL 12
APRIL 13
APRIL 14
TIME

RUN No. 54

Charge 448 grams of finely powdered spore material concentrate obtained by floating the standard sample ground through 100 mesh in 1.32 specific gravity ferrous chloride solution. The sample used for the separation contained 2.55% sulphur. The light portion after drying to constant weight at 100 C contained 4.00% sulphur. The ash content by ignition of one gram was found to be 23.6% and by calculation from the residue and its ash, 24.3%. As the residue was extremely difficult to remove from the retort the four grams difference in the ash present may easily be explained by scaling of the retort.
The retort was only half full. Switched on 11.40 a.m.
Room temperature 15 C. Barometer 771 m.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 6 & 4 m.l. respectively = 5.0 galls/ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.00	56	23		
12.30	166	63		
1.00	270	131		
1.15	311	168		
1.30	349	204		
1.45	385	242	2.5	2.0
2.00	415	272	4.5	4.0
2.05				5.5
2.10				7.0
2.15	442	304	12.0	10.3
2.20				13.5
2.25				17.3
2.30	462	333	32.0	21.0
2.35				24.4
2.40				26.3
2.45	480	372	64.0	28.5
2.50				28.5
2.55				28.0
3.00	498	420	99.0	26.3
3.05				25.8
3.10				24.1
3.15	513	444	125.0	23.2
3.20				21.2
3.25				18.0
3.30	531	463	135.0	10.4
3.35				6.2
3.40				4.0
3.45	545	482	136.0	3.6
4.00	557	497	136.00	2.5

Water condensed gallons per ton	5.0
Oil yield gallons per ton	136.0
Specific gravity of oil	0.921
Sulphur content of oil	2.43%
Saturation of oil	32%

Run No. 54 continued

Residue Data

Weight 159 grams Percentage of shale 35.5%

Proximate analysis of residue

Volatiles 7.0% Fixed carbon 24.3% Ash 68.7% Sulphur 2.82%

Sulphur distribution in products of distillation

Residue	25.2%
Oil	33.8
Hydrogen sulphide	40.4
Other gases and loss	0.6
	100.0

General Data

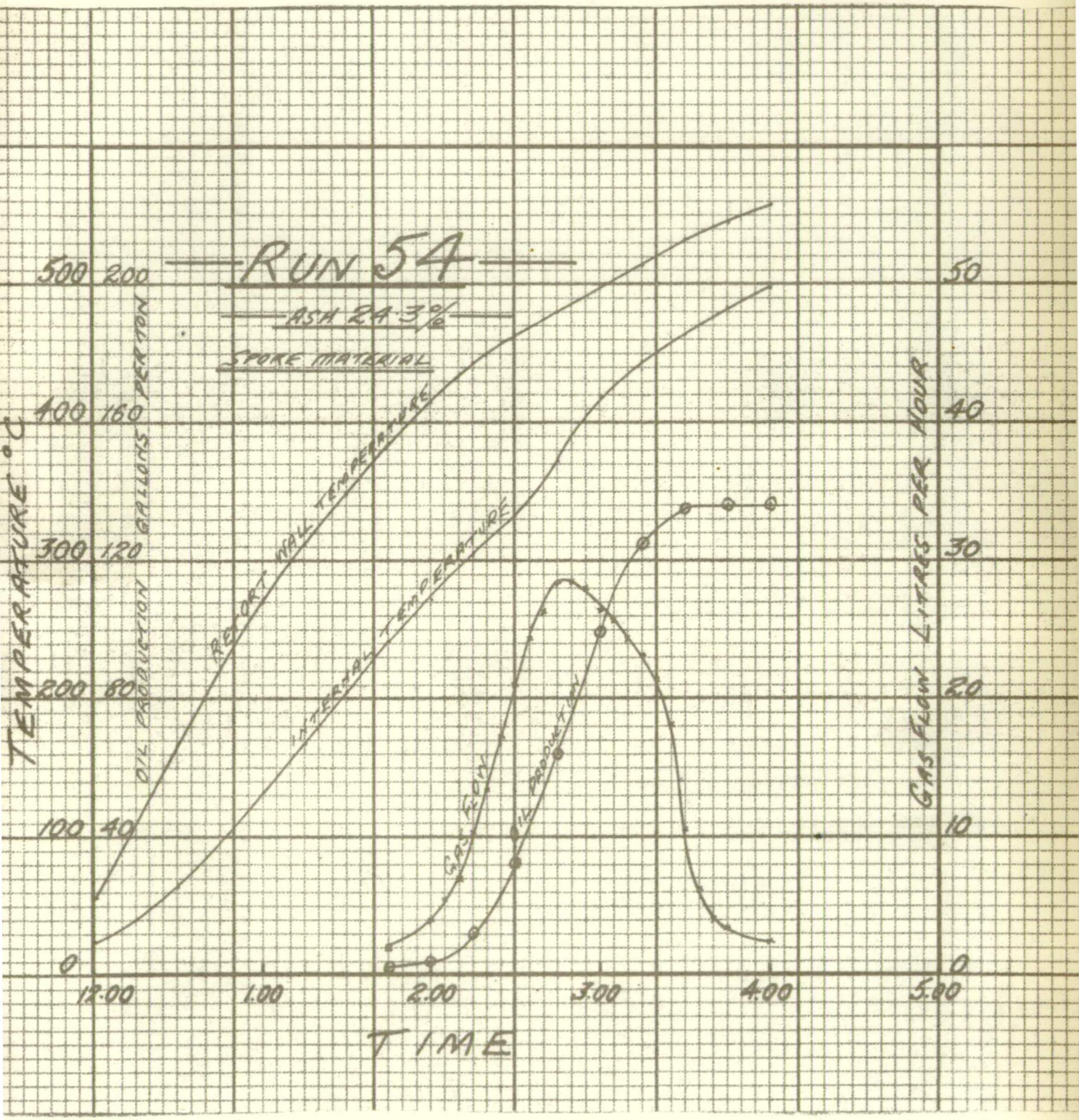
Ash/shale ratio		0.243	
Kerogen percentage		75.7	
Distillation Index		1.80	
Rate of heating in distillation range		115	deg.C/hour
Total time of oil production		2.0	hours
Maximum rate of oil production		140	galls/ton/hour
do. per % kerogen		1.85	do.
Gas production	Carbon dioxide	118	cu.ft./ton N.T.P.
	Hydrogen sulphide	405	do.
	Scrubbed gas	2470	do.
	Total gas	2993	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	24.30	3.30
Volatiles in residue	2.48	
Fixed carbon in residue	8.62	11.40
Oil	55.70	73.50
Water	2.23	2.95
Carbon dioxide	0.65	0.85
Hydrogen sulphide	1.72	2.30
Other gases and loss	4.30	5.70
	100.00	100.00

Note.

This concentrated spore material fuses in distillation and the residue that is left forms an exceedingly hard dense deposit similar to gas carbon.


RUN 54
ASH 24·3%
STOKE MATERIAL
TEMPERATURE °C.
OIL PRODUCTION GALLONS PER TON
GAS FLOW LITRES PER HOUR
REACTOR WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
500
400
300
200
100
0
200
160
120
80
40
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00
5.00
TIME

RUN No. 55

Charge 1120 grams dried to constant weight at 100 C of residue from the flotation of the concentrate distilled in Run 54. This residue was in fine powder and yielded no float on retreatment with 1.32 sp.gr. ferrous chloride solution but was found later to yield a float with carbon tetrachloride. Subsequent work showed that it consisted of 8% ash-free spore material and 92% spore-free residue containing another species of organic matter. It was therefore still a composite material. Ash 78.9%, sulphur 1.70%. The sample had lost its sulphate sulphur by solution.
The retort was full of charge. Room temperature 17 C, Bar. 760
Switched on 11.30 a.m., put retort in 12.00 noon, cut off 5.00 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 4 & 3 m.l. resp. = 1.4 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.30	204	75		
1.00	291	136		
1.15	327	177		
1.30	359	213	0.4	0.5
1.45	388	255	0.8	1.4
2.00	4.15	290	1.4	2.8
2.05				4.0
2.10				4.5
2.15	437	325	2.8	7.1
2.20				10.0
2.26				13.5
2.30	456	355	6.8	15.2
2.35				17.0
2.40				18.0
2.45	474	379	12.6	19.0
2.50				19.3
2.55				19.5
3.00	488	395	17.2	19.5
3.05				19.3
3.10				19.0
3.15	506	415	22.0	18.5
3.20				17.3
3.25				16.2
3.30	519	433	24.6	15.0
3.35				14.0
3.40				13.0
3.45	532	461	26.0	12.8
3.50				11.8
3.55				10.4
4.00	544	483	26.2	10.0
4.05				9.0
4.10				7.2
4.15	554	500	26.4	6.0

Run No. 55 continued

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
4.20				5.0
4.25				4.0
4.30	566	523	26.6	4.0
4.45	580	531	26.6	3.0
5.00	583	540	26.6	2.5

Water condensed gallons per ton	4.8
Oil yield gallons per ton	26.6
Specific gravity of oil	0.915
Sulphur content of oil	2.23
Saturation of oil	32%
Distillation analysis not determined	

Residue Data

Weight 951 grams Percentage of charge 84.9%

Proximate analysis of residue

Volatiles 3.8% Fixed carbon 3.35% Ash 92.85% Sulphur 1.37%

Sulphur distribution in products of distillation

Residue	68.3%
Oil	14.1
Hydrogen sulphide	15.9
Other gases and loss	1.7
	100.0

General Data

Ash/shale ratio		0.789	
Kerogen percentage		21.1	
Distillation Index		1.26	
Rate of heating in distillation range		85	deg.C/hour
Total time of oil production		2.5	hours
Maximum rate of oil production		23	galls/ton/hour
do. per % kerogen		1.09	do.
Gas production	Carbon dioxide	58	cu.ft./ton N.T.P.
	Hydrogen sulphide	68	do.
	Scrubbed gas	1018	do.
	Total gas	1144	do.

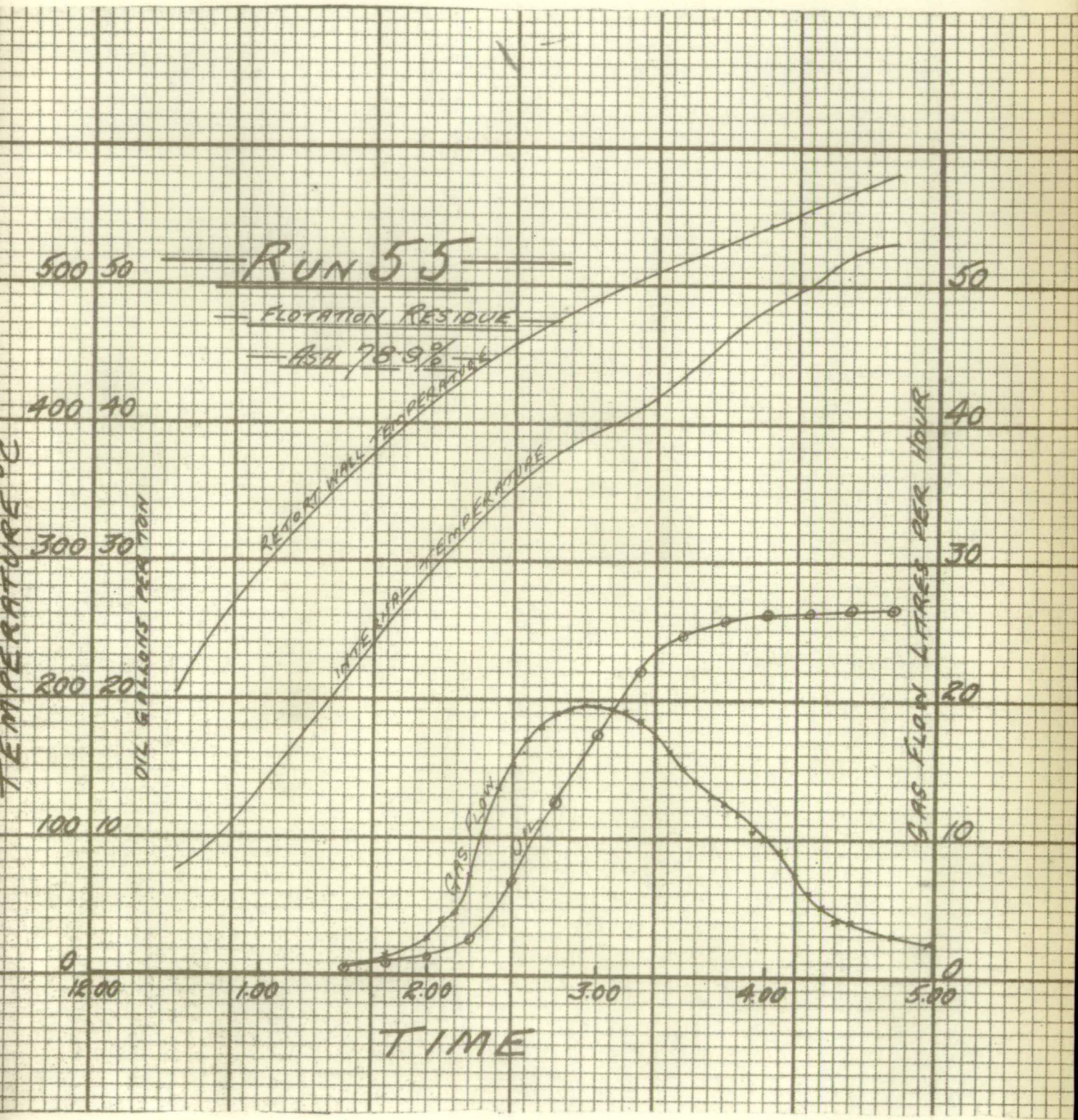
Run No. 55 continued

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	78.90%	
Volatiles in residue	3.44	16.30%
Fixed carbon in residue	2.55	12.10
Oil	10.76	50.95
Water condensed	2.14	10.15
Carbon dioxide	0.32	1.50
Hydrogen sulphide	0.29	1.40
Other gases and loss	1.60	7.60
	100.00	100.00

Note.

The residue from this run was not caked at all. The small proportion of spore material in which practically the whole of the caking power of a sample of shale resides was insufficient to produce any appreciable caking. The spore-free residue which was distilled in run 57 was so free from caking that after distillation it ran through an 80 mesh sieve without any crushing at all. The distillation from Run 54 is in marked contrast to this as the residue was so strongly caked that it took several hours to quantitatively remove the residue from theretort.


RUN 55
FLOTATION RESIDUE
ASH 78.9%
TEMPERATURE °C
OIL GALLONS PER HOUR
GAS FLOW LITRES PER HOUR
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
GAS FLOW
OIL
500
400
300
200
100
0
50
40
30
20
10
0
12.00
1.00
2.00
3.00
4.00
5.00
TIME

RUN No. 56

Charge 1120 grams of sample from the Tasmanite Shale Oil co. to check up with the operation of the Crozier retort. Size ¼" thickness flakes, ash 71.7%, dried to constant weight at 100 C.
Room temperature 11 C. Barometer 770 m.m.
Switched on 12.30 p.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 4 & 3 m.l. = 1.4 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
12.30	14	14		
2.30	332	257	0.2	
2.45	355	291	0.6	0.5
3.00	378	318	1.0	2.0
3.15	399	347	1.8	4.5
3.25				6.0
3.30	416	367	3.0	6.8
3.35				7.2
3.40				8.0
3.45	434	388	6.6	10.0
3.50				10.8
3.55				12.0
4.00	449	403	12.4	13.3
4.05				14.3
4.10				15.2
4.15	463	417	21.4	16.5
4.20				17.3
4.25				17.5
4.30	476	431	30.4	17.5
4.35				17.4
4.40				17.0
4.45	488	449	37.6	15.3
4.50				14.0
4.55				12.5
5.00	501	470	41.2	11.3
5.05				10.3
5.15	515	487	43.0	8.0
5.20				6.8
5.30	526	506	43.5	5.0
5.45	536	519	43.5	3.4

Water condensed gallons per ton	2.6
Oil yield gallons per ton	43.5
Specific gravity of oil	0.919
Sulphur content of oil	2.36%
Saturation of oil	35%

Distillation analysis not determined

Residue Data

Weight 879 grams Percentage of shale 78.5%

Run No. 56 continued

Proximate analysis of residue

Volatiles 5.15% Fixed carbon 3.45% Ash 91.40% Sulphur 1.54%

Sulphur distribution in products of distillation

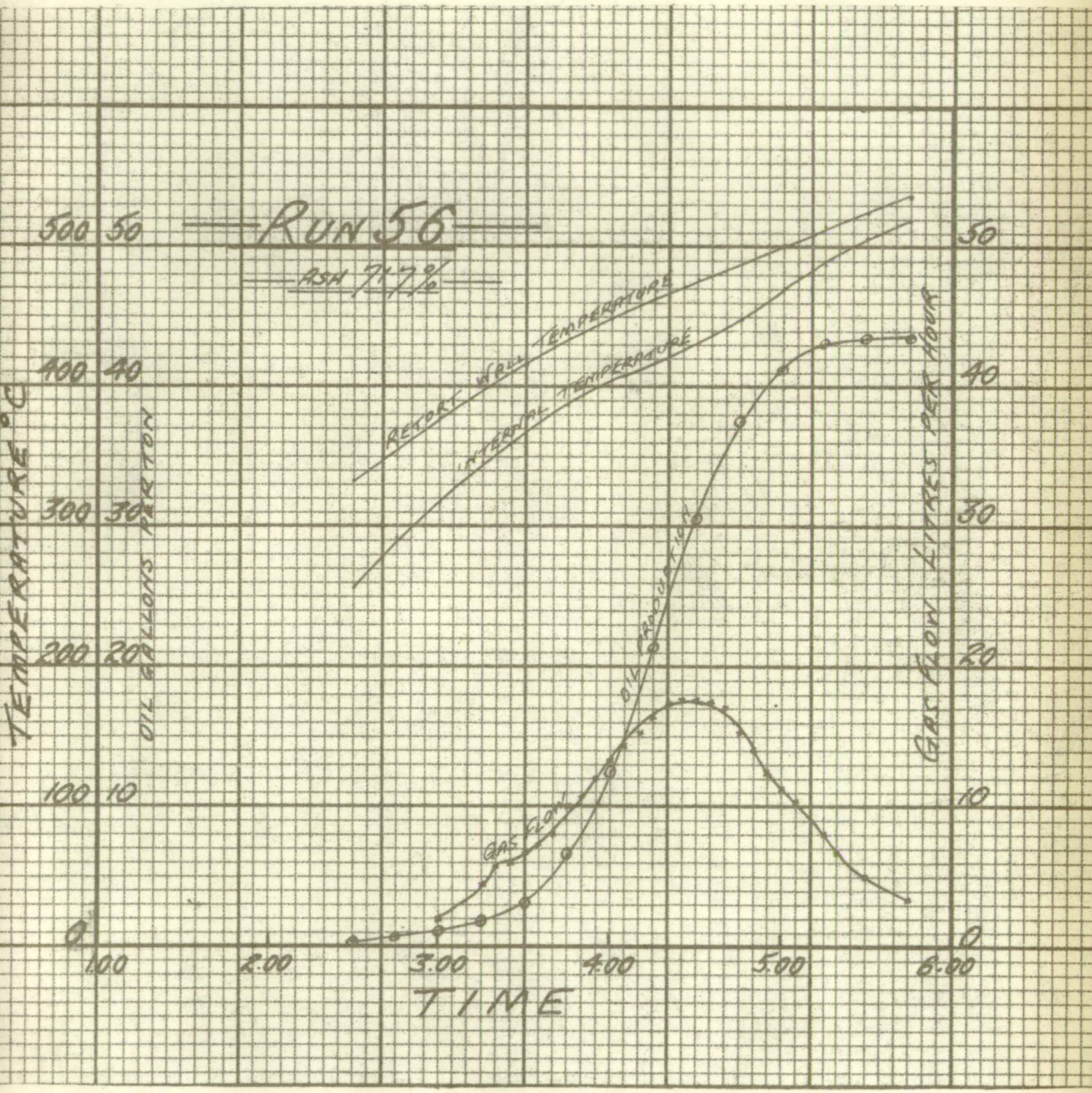
Residue 13.55 grams, Oil 4.65 grams, Hydrogen sulphide 12.1 grams
Total recovery 30.3 grams = 2.70% on the shale.

General Data

Ash/shale ratio		0.717	
Kerogen percentage		28.3	
Distillation Index		1.53	
Rate of heating in distillation range		70	deg.C/hour
Total time of oil production		2.5	hours
Maximum rate of oil production		36	galls/ton/hour
do. per % kerogen		1.27	do.
Gas production	Carbon dioxide	37	cu.ft./ton N.T.P.
	Hydrogen sulphide	272	do.
	Scrubbed gas	873	do.
	Total gas	1182	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	71.70	
Volatiles in residue	4.05	14.30
Fixed carbon in residue	2.71	9.55
Oil	17.60	62.25
Water condensed	1.16	4.10
Carbon dioxide	0.20	0.70
Hydrogen sulphide	1.15	4.05
Ohter gases and loss	1.43	5.05
	100.00	100.00


RUN 56
ASH 7.7%
TEMPERATURE °C
OIL GALLONS PER HOUR
GAS CUBIC FEET PER HOUR
REACTOR WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL THROUGHPUT
GAS
CO2
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00
TIME

RUN No 57

Charge 672 grams of the heavier material from a carbon tetrachloride separation of pulverised standard sample, ash 85.5%, sulphur content 2.07%. This separation was carried out on very finely pulverised shale and this portion which sank in the tetrachloride appeared under the microscope to be free from spore cases. The sample was dried to constant weight at 100 C.
Room temperature 11 C. Barometer 770 m.m.
Switched on 12.20 p.m.
All gas prior to 2.40 p.m. was lost through an accident but it would consist almost entirely of carbon dioxide and contain no hydrogen sulphide.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 2 & 1 m.l. = 1.0 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR
2.30	349	282		
2.45	376	318	0.3	0.7
3.00	396	348	0.8	0.7
3.10				1.4
3.15	413	370	1.7	2.1
3.20				2.6
3.25				2.8
3.30	431	394	3.0	3.1
3.35				3.5
3.40				4.2
3.45	444	415	4.7	4.8
3.50				4.9
3.55				5.3
4.00	456	430	7.0	5.7
4.05				5.3
4.10				5.1
4.15	466	441	9.3	5.3
4.20				5.1
4.25				5.1
4.30	477	458	10.6	5.1
4.35				4.9
4.40				4.7
4.45	489	471	12.0	4.5
4.50				4.2
4.55				2.8
5.00	499	485	13.0	3.5
5.05				2.8
5.10				3.1
5.15	509	496	13.3	2.1
5.30	521	507	13.5	1.4
5.45	533	521	13.5	0.7

Run No. 57 continued

Residue Data

Weight 614 grams Percentage of shale 91.4%

Proximate analysis of residue

Volatiles 5.5% Fixed carbon 1.0% Ash 93.5% Sulphur 2.15%

Sulphur distribution in products of distillation

Residue	95.0%
Oil	4.8
Hydrogen sulphide	0.0
Other gases and loss	0.2
	100.0

Water condensed gallons per ton	5.2
Oil yield gallons per ton	13.5
Specific gravity of oil	0.911
Sulphur content of oil	1.85
Saturation of oil	38%

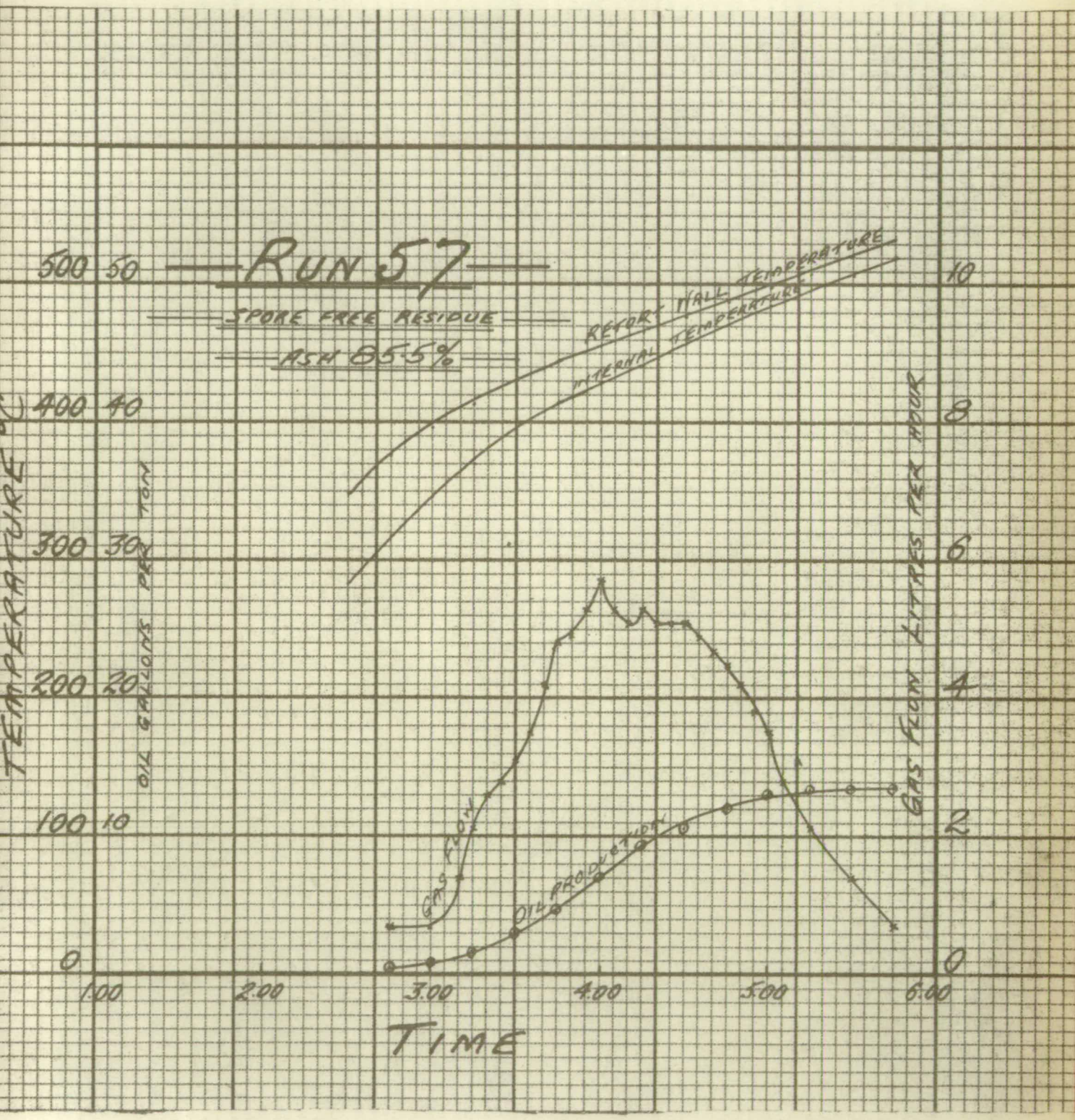
Distillation analysis not determined

General Data

Ash/shale ratio		0.855	
Kerogen percentage		14.5	
Distillation Index		0.93	
Rate of heating in distillation range		65	deg.C/hour
Total time of oil production		2.5	hours
Maximum rate of oil production		9.2	galls/ton/hour
do. per % kerogen		0.63	
Gas production	Carbon dioxide	45	cu.ft./ton N.T.P.
	Hydrogen sulphide	nil	
	Scrubbed gas	490	do.
	Total gas	535	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	85.50%	
Volatiles in residue	5.02	34.60%
Fixed carbon in residue	0.91	6.30
Oil	5.41	37.30
Water condensed	2.30	15.85
Carbon dioxide	0.25	1.75
Hydrogen sulphide	0.00	0.00
Other gases and loss	0.61	4.20
	100.00	100.00


RUN 57
SPORE FREE RESIDUE
ASH 0.55%
REFORMER WALL TEMPERATURE
MATERIAL TEMPERATURE
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
GAS FLOW
OIL PRODUCTION
500
400
300
200
100
0
50
40
30
20
10
10
8
6
4
2
0
1.00
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 58

Charge 1120 grams of sample representing retort feed from Tasmanite Shale Oil Co's plant, June 1932. This sample was from the Goliath Portland Cement Co's mine, New Tunnel and comprised the whole seam including the middle band. Ash content 80.4%, sulphur 2.55%. Dried to constant weight at 100 C.
Room temperature 11 C. Barometer 768 m.m.
Switched on 11.50 a.m.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches 3 & 2 m.l. resp. = 1.0 gallon per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS PER TON	GAS FLOW
12.20	84	29		
1.35	307	201		
2.00	361	273	0.2	0.5
2.15	384	307	0.4	0.7
2.20				0.7
2.25				2.1
2.30	407	340	0.8	3.5
2.35				4.2
2.40				4.9
2.45	427	353	1.8	5.6
2.50				6.0
2.55				6.4
3.00	444	385	4.0	7.0
3.05				7.3
3.10				9.0
3.15	460	405	8.4	10.0
3.20				10.3
3.25				10.8
3.30	472	419	13.2	10.8
3.35				10.8
3.40				10.8
3.45	483	433	18.2	10.6
3.50				10.3
3.55				10.1
4.00	496	450	21.0	10.0
4.05				9.5
4.10				9.0
4.15	505	474?	22.6	8.3
4.30	514	486	24.0	6.8
4.35				6.4
4.45	524	502	24.6	5.3
5.00	534	509	25.2	4.9
5.15	542	521	25.5	2.5
5.30	548	529	25.5	1.4

Run No. 58 continued

Water condensed gallons per ton	2.4
Oil yield gallons per ton	25.5
Specific gravity of oil	0.912
Sulphur content of oil	2.16%
Saturation of oil	37%

Distillation analysis not determined

Residue Data

Weight 968 grams Percentage of shale 86.4%

Proximate analysis of residue

Volatiles 5.2% Fixed carbon 1.7% Ash 93.1% Sulphur 1.55%

Sulphur distribution in products of distillation

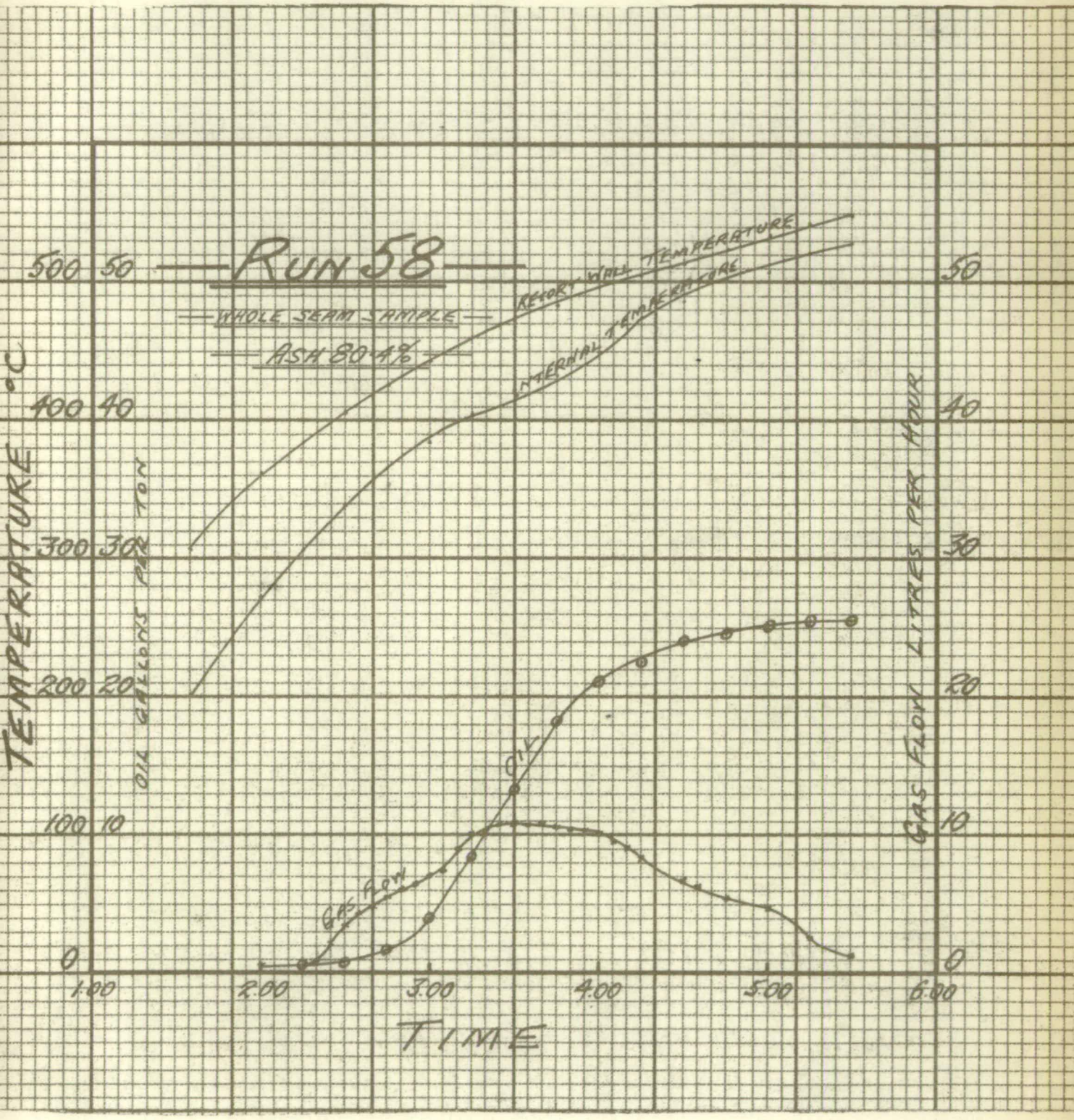
Residue	52.55%
Oil	8.75
Hydrogen sulphide	28.80
Other gases and loss	9.90
	100.00

General Data

Ash/shale ratio		0.804	
Kerogen percentage		19.6	
Distillation Index		1.30	
Rate of heating in distillation range		70	deg.C/hour
Total time of oil production		3.0	hours
Maximum rate of oil production		20	galls/ton/hour
do. per % kerogen		1.02	do.
Gas production	Carbon dioxide	43	cu.ft./ton N.T.P.
	Hydrogen sulphide	183	do.
	Scrubbed gas	652	do.
	Total gas	878	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	80.40%	
Volatiles in residue	4.50	22.95
Fixed carbon in residue	1.47	7.50
Oil	10.31	52.55
Water condensed	1.07	5.45
Carbon dioxide	0.24	1.25
Hydrogen sulphide	0.78	4.00
Other gases and loss	1.23	6.30
	100.00	100.00


RUN 58
WHOLE SEAM SAMPLE
ASH 80·4%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL
GAS FLOW
TEMPERATURE °C
OIL GALLONS PER TON
GAS FLOW LITRES PER HOUR
TIME
500
400
300
200
100
0
50
40
30
20
10
0
1.00
2.00
3.00
4.00
5.00
6.00

RUN No. 59

Charge 1120 grams standard sample, dried to constant weight at 100C, ash 66.2%, in ¼" thickness flakes. Switched on 9.00 a.m. Room temperature 10 C. Barometer 772 m.m.
Distilled slowly under low pressure at about the same rate of heating as Run 52 to compare the action of steam in lowering the partial pressure of the oil vapours with simple low pressure.
The apparatus was arranged in the following order:-
Usual condensers with primary and secondary receivers
Manometer connection
Oil scrubber - 100 m.l. cylinder containing 60 m.l. lighting kerosene - about 12 cm bubbling depth.
Trap 600 m.l. flask empty
Hydrogen sulphide scrubber - 1 litre flask 600 ml. 25% NaOH soln.
Arnold absorption bulb as trap also containing 25% NaOH soln.
Non-return valve in case of water pressure failure
Water trap
Water suction pump
Receiver with water and gas deliveries
Oil scrubber 100 m.l. cylinder 50 m.l. kerosene 10 cm. depth
Oil scrubber 250 m.l. cylinder 90 m.l. kerosene 10 cm. depth
Capillary flow meter.

The order given is that of gas flow. By this arrangement it was hoped to perform the final scrubbing at atmospheric pressure but this was thwarted by a small leak developing in the retort capping allowing ingress of diluting air of fully the volume of the retort gas. The recorded figures for the gas production were thus rendered valueless and condensation made more difficult at every stage. Allowing for the extra spirit carried away in the gas stream the general results seemed so similar to those of the slow steam distillation Run 52 that a repeat distillation was not carried out. The use of lower pressure in the retort with the lesser time of contact of oil vapours and heated residue together with the lower temperature necessary gave, in spite of the poorer spirit recovery, an increased oil yield compared with distillation at the same rate of heating at atmospheric pressure. The use of steam however secures the same conditions in the retort without causing any serious condensation difficulties. No definite adverse effect of the steam as such can be traced except in giving more unsaturated oils and a lesser proportion of the lighter oils.

The absolute pressure maintained at the manometer connection averaged a little under 12 cm. of mercury say 2.5 lbs per square inch. For about 30 minutes when the oil production was at a maximum the pressure rose to 15 cm. of mercury but for the remainder of the distillation the pressure was steady at slightly under 12 cm.

Run No. 59 continued

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON
10.25	237	141	
10.45	283	199	
11.00	314	239	
11.15	343	279	0.2
11.30	355	314	0.4
11.45	363	332	0.8
12.00	370	348	1.2
12.15	380	356	1.6
12.30	384	365	3.0
12.45	389	371	4.4
1.00	396	378	5.6
1.15	405	385	7.4
1.30	411	390	9.4
1.45	419	397	12.0
2.00	426	403	16.0
2.15	431	410	20.6
2.30	438	417	26.4
2.45	446	425	31.6
3.00	454	433	37.0
3.15	461	441	41.0
3.30	466	451	44.8
3.45	471	460	46.6
4.00	474	463	47.6
4.15	481	469	48.2
4.30	488	475	48.6
4.45	497	484	48.8
5.00	507	491	49.0
5.15	519	502	49.0
5.30	532	519	49.0

Water condensed gallons per ton	6.0
Oil yield gallons per ton	49.0
Specific gravity of oil (in receivers only)	0.947
Sulphur content of oil	2.38%
Saturation of oil	23%

Distillation analysis of oil not determined

Residue Data

Weight 823.5 grams Percentage of shale 73.5%

Proximate analysis of residue

Volatiles 5.4% Fixed carbon 4.55% Ash 90.05% Sulphur 1.97%

Run No. 59 continued

Sulphur distribution in products of distillation

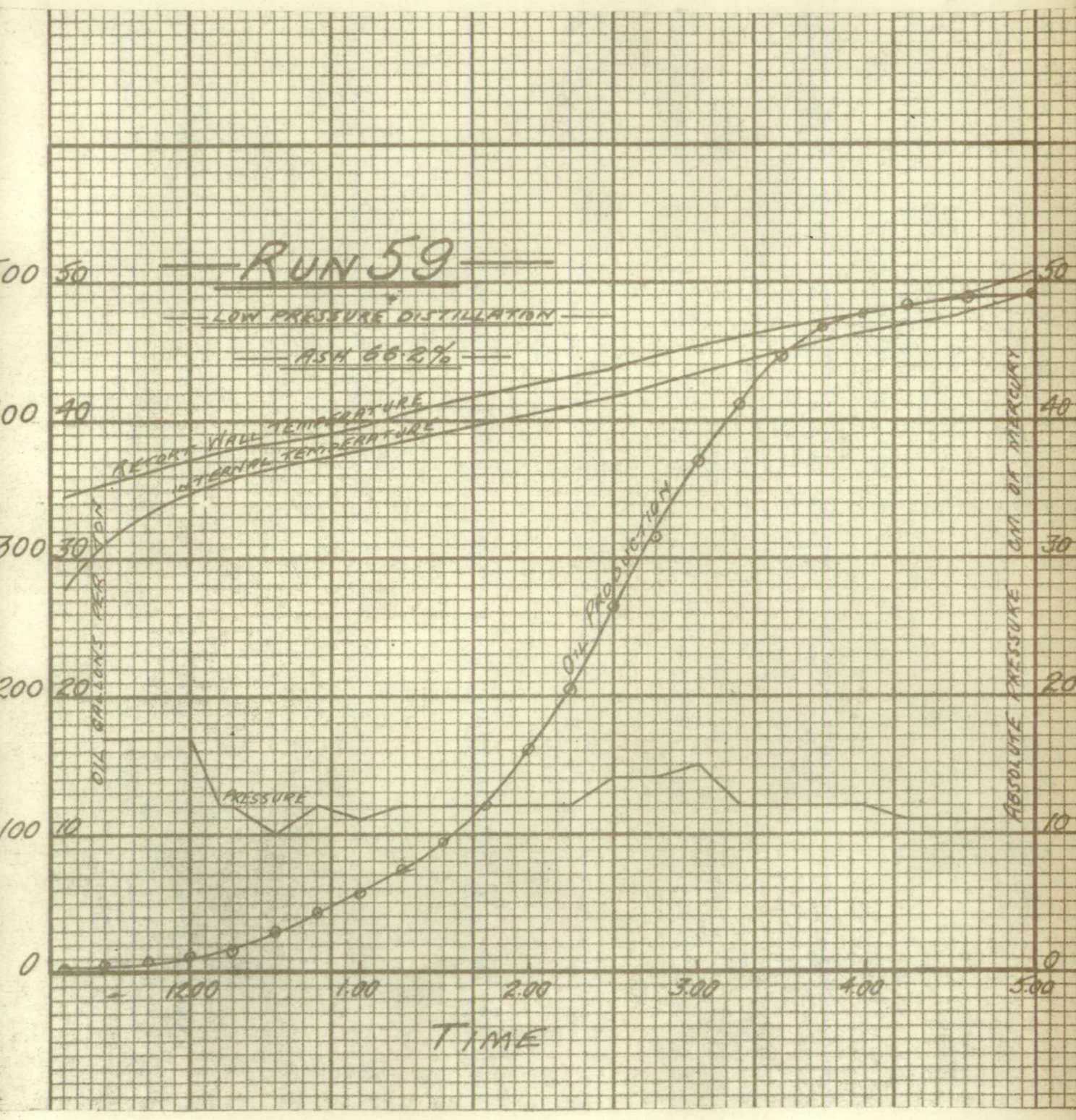
Residue	55.7%
Oil	18.9
Hydrogen sulphide	22.5
Other gases and loss	2.9
	100.0

General Data

Ash/shale ratio		0.662	
Kerogen percentage		33.8	
Distillation Index		1.45	
Rate of heating in distillation range		27	deg.C/hour
Total time of oil production		5.5	hours
Maximum rate of oil production		22	galls/ton/hour
do. per % kerogen		0.65	do.
Gas production	Carbon dioxide	77	cu.ft./ton N.T.P.
	Hydrogen sulphide	147	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.20%	
Volatiles in residue	3.97	11.70%
Fixed carbon in residue	3.35	9.90
Oil	20.60	60.95
Water condensed	2.68	7.95
Carbon dioxide	0.42	1.25
Hydrogen sulphide	0.62	1.85
Other gases and loss	2.16	6.40
	100.00	100.00


RUN 59
LOW PRESSURE DISTILLATION
ASH 66.2%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
PRESSURE
OIL EVOLVED PER HOUR
ABSOLUTE PRESSURE mm OF MERCURY
TIME
12.00
1.00
2.00
3.00
4.00
5.00
0
10
20
30
40
50
100
200
300
400

RUN No. 60

Charge 1120 grams standard sample, ash 66.1%, dried to constant weight at 100 C, in ¼" thickness flakes.
Room temperature 11 C. Barometer 764 m.m.
Distilled under low pressure with the same arrangement of apparatus as Run 59 but with 60 C rate of heating.
A faulty union which could not be replaced without having one specially made allowed entry of air partially spoiling the value of the run as regards the condensation of the oil.
Oil scrubber catches in order of flow 10, 3, & 2.5 m.l. = 3.1 g/ton

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	ABS. PRESSURE CM. OF MERCURY
2.30	284	201		
2.48	320	249		
3.00	344	278		11
3.15	367	314	0.6	13
3.30	392	345	1.2	11
3.45	416	368	2.0	11
4.00	432	390	6.4	16
4.15	444	409	14.6	17
4.30	453	418	24.2	20
4.45	463	427	35.2	20
5.00	472	438	44.4	19
5.15	480	452	49.2	18
5.30	486	463	50.8	17
5.45	497	473	51.6	16
6.00	504	484	51.6	16
6.15	517	496	51.6	

Water condensed gallons per ton	5.4
Oil yield gallons per ton	51.6
Specific gravity of oil	0.940
Sulphur content of oil	2.46
Saturation of oil	22%

Distillation analysis not determined

Residue Data

Weight 819.5 grams Percentage of shale 73.3%

Proximate Analysis of residue

Volatiles 6.0% Fixed carbon 3.75% Ash 90.25% Sulphur 1.93%

Run No. 60 continued

Sulphur distribution in products of distillation

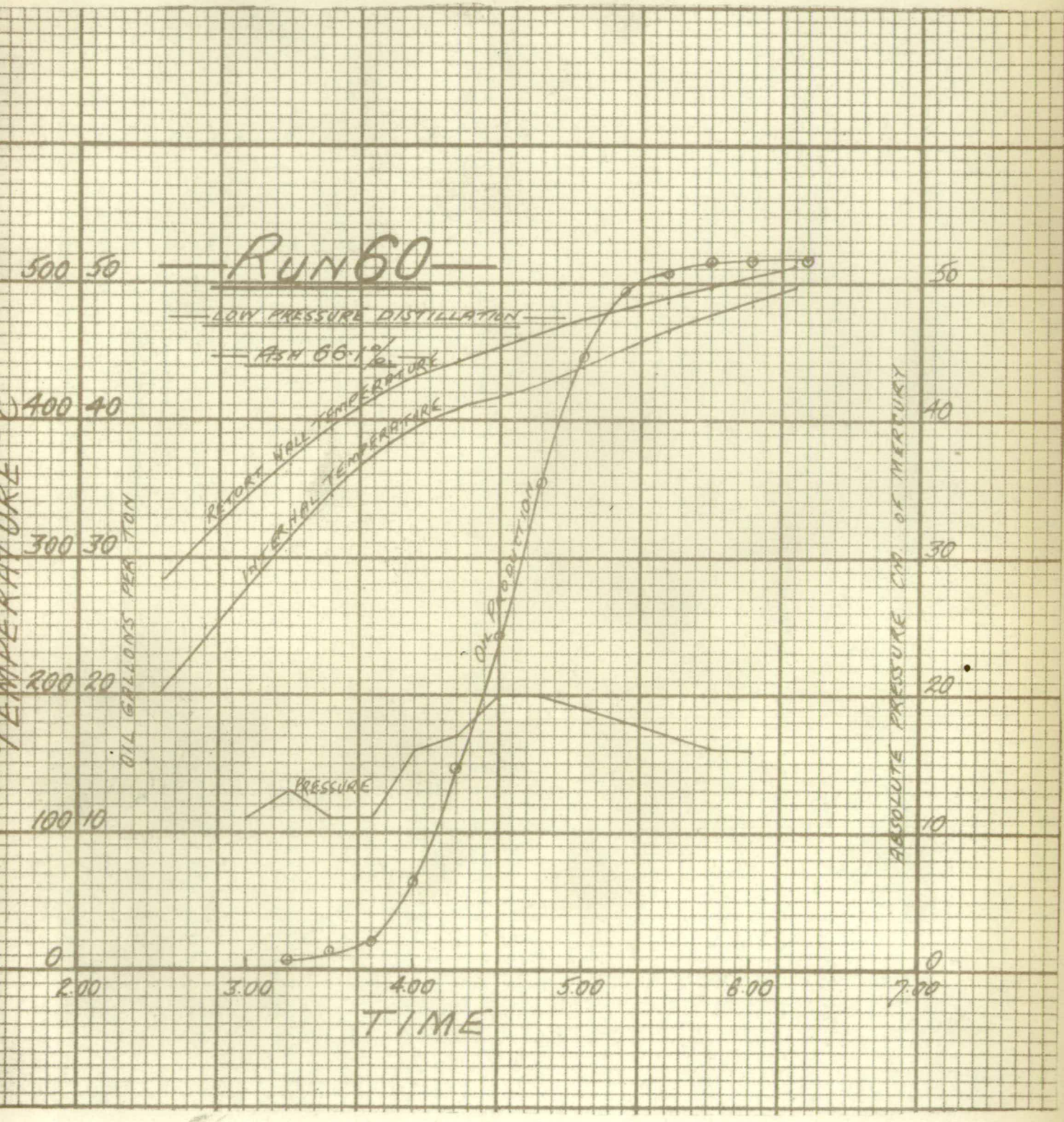
Residue	54.3%
Oil	20.4
Hydrogen sulphide	20.85
Other gases and loss	4.45
	100.0

General Data

Ash/shale ratio		0.661	
Kerogen percentage		33.9	
Distillation Index		1.52	
Rate of heating in distillation range		60	deg.C/hour
Total time of oil production		2.5	hours
Maximum rate of oil production		44	galls/ton/hour
do. per % kerogen		1.30	do.
Gas production	Carbon dioxide	42	cu.ft./ton N.T.P.
	Hydrogen sulphide	136	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	66.10%	
Volatiles in residue	4.39	12.95%
Fixed carbon in residue	2.74	8.10
Oil	21.50	63.45
Water condensed	2.41	7.10
Carbon dioxide	0.24	0.70
Hydrogen sulphide	0.58	1.70
Other gases and loss	2.04	6.00
	100.00	100.00


RUN 60
LOW PRESSURE DISTILLATION
ASH 66.1%
RETORT WALL TEMPERATURE
INTERNAL TEMPERATURE
OIL PRODUCTION
PRESSURE
TEMPERATURE
OIL GALLONS PER TON
ABSOLUTE PRESSURE CM OF MERCURY
500
400
300
200
100
0
50
40
30
20
10
0
2.00
3.00
4.00
5.00
6.00
7.00
TIME

TABULATED DISTILLATION RESULTS

Number of Run	10	11	12	13	14	15	16	17	18
Particle size	½"	½"	½"	½"	½"	½"	½"	½"	½"
Water condensed	5	5	5	-	-	4.6	4.0	5.4	5.4
Oil data									
Gallons per ton	53	48	49.6	51.2	51.8	52.6	52.4	50.0	51.0
Sp. Gr.	0.925	0.905	0.945	0.952	0.952	0.925	0.930	0.926	0.931
Sulphur %	2.47	2.43	2.30	2.38	2.61	2.40	2.31	2.36	2.26
Saturation %	-	-	-	14	14	26	22	27	27
Dist. Analysis									
Below 150 C	11.4%	14.7%	9.8%	12.0%	11.1%	11.1%	8.4%	12.3%	11.5%
150 C - 200 C	9.7%	10.3	10.0	7.5	7.8	10.7	10.7	10.2	10.1
200 C - 250 C	11.0	10.5	11.3	10.8	9.7	9.6	10.8	10.8	10.1
250 C - 300 C	12.6	12.5	12.7	13.1	11.4	12.7	11.7	14.1	12.8
Residuum	55.3	52.0	56.2	56.6	60.0	55.9	58.4	52.6	55.5
Residue data									
Weight in grams	881	836	824	824	824	816.5	812	823	944?
% of shale	73.05	74.6	73.6	73.6	73.6	72.9	72.5	73.5	-
Prox. Analysis									
Volatiles 900 C	4.6%	5.6%	3.95%	5.45	5.3%	4.6%	4.0%	-	4.75%
Fixed carbon	4.35	5.2	5.1	4.0	3.8	4.25	4.2	-	1.15
Ash	91.05	89.2	90.95	90.55	90.9	91.15	91.8	-	94.1
Sulphur	1.72	1.73	1.92	1.70	1.70	1.65	1.79	1.59	2.28
S distribution									
In residue	48.1%	49.7%	54.3%	48.0%	48.1%	46.3%	50.0%	45.0%	73.8%
In oil	20.5	18.4	18.2	19.7	22.0	19.9	19.5	18.5	17.7
In H_2S	-	-	-	-	-	30.8	26.8	26.7	6.4
Other gases etc	-	-	-	-	-	3.8	3.7	9.8	2.1
General data									
Ash/shale ratio	0.666	0.666	0.668	0.666	0.668	0.665	0.665	0.665	0.665
Kerogen %	33.4	33.4	33.2	33.4	33.2	33.5	33.5	33.5	33.5
Dist. Index	1.58	1.44	1.50	1.53	1.56	1.57	1.57	1.49	1.52
Rate of heating	140	50	120	140	120	170	140	150	160
Oil prodn. time	1.5	5.0	2.0	1.5	1.5	1.5	1.5	1.75	1.5
Max. rate O.P.	72	52	80	-	-	90	80	8 4	75
Do. per % kero.	2.16	1.56	2.40	-	-	2.69	2.38	2.50	2.24
Carbon dioxide						44	77	116	16
H_2S						156	185	185	42
Scrubbed gas									977
Total gas									1035
Ammon. sulphate	1.14	0.7	-	1.61	1.80				
Weight distribn									
Vol. in res.	10.05	12.5	8.7	12.0	11.75	10.0	8.65		
F. C. in res.	9.5	11.6	11.3	8.85	8.45	9.25	9.1	20.9	
Oil	65.55	58.05	63.0	65.05	66.25	64.9	64.85	61.5	62.5
Water	6.65	6.7	6.7	-	-	6.1	5.3	7.2	7 2
CO_2						0.7	1.25	1.9	
H_2S						1.85	2.35	2.2	
Gases etc.	8.25	11.15	10.3	14.1	13.55	7.2	8.5	6.3	
Number of Run	10	11	12	13	14	15	16	17	18

TABULATED DISTILLATION RESULTS

Number of Run	19	20	21	22	23	24	25	26	27
Particle size	½"	-20	-20	½"	3/16"	3/16"	3/4"	3/16"	-20
Water condensed	5.0	5.2	5.0	6.0	5.0	6.0	5.0	5.2	7.0
Oil data									
Gallons per ton	48.2	50.6	51.4	50.4	52.3	51.0	51.0	41.6	47.2
Sp. Gr.	0.903	0.909	0.925	0.922	0.922	0.927	0.924	0.897	0.928
Sulphur %	2.19%	2.29	2.37	2.52	2.52	2.59	2.43	2.29	2.32
Saturation %	36	28	18	21	27	27	21	39	22
Dist. Analysis									
Below 150 C	15.1%	14.4%	13.1%	11.8%	11.0%	13.0%	12.3%	14.7%	13.2
150 C - 200 C	10.7	10.6	9.2	10.1	9.6	10.5	10.3	13.9	11.0
200 C - 250 C	11.0	10.8	11.3	11.0	10.8	9.2	10.6	11.7	10.7
250 C - 300 C	12.7	13.4	10.9	11.5	11.0	13.8	12.0	15.6	12.8
Residuum	50.5	50.8	55.5	55.6	57.6	53.5	54.8	44.1	52.3
Residue data									
Weight in grams	833	825	813	820	807	807	817	859	820
% of shale	74.3	73.6	72.6	73.1	72.0	72.0	73.0	76.6	73.2
Prox. Analysis									
Volatiles 900 C	4.8%	5.15	3.85	4.2%	4.65	4.7%	4.95	5.45	4.6%
Fixed carbon	5.6	5.25	4.60	4.45	4.25	4.15	3.90	6.75	4.7
Ash	89.6	89.6	91.55	91.35	91.1	91.15	91.15	87.8	90.7
Sulphur	1.69	1.93	2.01	1.76	1.61	1.86	1.67	1.83	2.09
S distribution									
In residue	48.2%	54.7%	56.1%	49.5%	44.6%	51.5%	46.8%	53.9%	58.9%
In oil	16.8	18.0	17.2	20.1	20.3	20.3	19.1	14.4	16.7
In H_2S	29.4	22.8	30.5	27.4	30.9	28.0	27.4	27.1	20.8
Other gases etc	5.6	4.5	-3.8	3.0	4.2	0.2	6.7	4.6	3.6
General data									
Ash/shale ratio	.666	.660	.665	.668	.656	.656	.665	.672	.665
Kerogen %	33.4	34.0	33.5	33.2	34.4	34.4	33.5	32.8	33.5
Dist. Index	1.44	1.49	1.53	1.52	1.52	1.48	1.52	1.27	1.41
Rate of heating	~~%~~38	45	140	175	165	260	280	10	200
Oil prodn. time	5.0	3.5	1.75	1.5	1.25	1.0	1.0	12.0	1.25
Max. rate O.P.	26	34	65	80	82	103	144	10	70
Do. per % kero.	0.78	1.00	1.94	2.41	2.38	3.00	4.30	0.31	2.09
Carbon dioxide	63	108	73	62	55	113	77	65	77
H2 S	192	149	197	179	202	183	179	177	136
Scrubbed gas	1395	1202	1248	1008	1018	1057	1057	1847	1302
Total gas	1650	1459	1518	1249	1275	1353	1313	2089	1515
Weight distribn									
Vol. in residue	10.7%	10.9%	8.35	9.3%	9.75	9.8%	10.8%	12.75	10.0%
F.C. in residue	12.45	11.35	9.95	9.75	8.9	8.7	8.8	15.7	10.25
Oil	58.15	60.6	62.7	62.4	62.5	61.35	62.7	50.9	58.3
Water	6.7	6.85	6.65	8.05	6.5	7.8	6.65	7.1	9.3
CO_2	1.05	1.80	1.20	1.05	0.85	1.80	1.25	1.10	1.25
H_2S	2.40	1.85	2.50	2.25	2.45	2.25	2.25	2.30	1.70
Gases etc.	8.55	6.65	8.65	7.20	9.05	8.30	7.55	10.15	9.20
Number of Run	19	20	21	22	23	24	25	26	27

TABULATED DISTILLATION RESULTS

Number of Run	28	29	30	31	32	33	34	35	36
Particle size	3/16"	½"	3/16"	3/16"	½"	½"	½"	½"	½"
Water condensed	6.0	5.0	6.6	5.0	5.6	6.0	4.0	2.8	1.5
Oil Data									
Gallons per ton	48.8	52.6	22.6	22.8	39.0	34.2	23.6	6.4	2.7
Sp. Gr.	.927	.926	.969	.969	.899	.892	.903	.909	.911
Sulphur %	2.37	2.41	3.20	2.96	2.32	2.52	0.65	2.28	2.48
Saturation %	22	26	28	26	39	39	50	34	40
Dist. Analysis									
Below 150 C	11.9%	11.1%	24.0%	24.0%	16.3%	23.6%	15.8%	n.d.	n.d.
150 C - 200 C	11.0	10.6	13.2	18.6	13.0	14.0	9.4		
200 C - 250 C	10.5	9.8	20.3	15.7	12.2	10.7	10.0		
250 C - 300 C	12.4	11.9	12.6	16.5	14.5	18.5	12.5		
Residuum	54.2	56.6	29.9	25.2	44.0	33.2	52.3		
Residue Data									
Weight in grams	817	807.5	841	837	826	842	974	1591	1636
% of shale	73.0	72.0	75.1	74.75	73.8	75.1	86.9	94.75	97.5
Prox. Analysis									
Volatiles 900 C	4.20	4.75	5.70	5.55	5.05	5.80	4.45	3.50	3.90
Fixed carbon	4.10	4.20	4.75	5.35	5.00	5.65	3.65	0.90	0.00
Ash	91.70	91.05	89.55	89.10	89.95	88.55	91.90	95.60	96.10
Sulphur	1.90	1.75	1.88	1.82	1.77	1.78	0.28	2.12	1.79
S distribution									
In residue	53.2%	48.4%	58.7%	52.4%	54.2%	57.3%	79.8%	n.d.	86.6%
In oil	17.6	19.4	9.5	10.3	13.4	13.2	20.2		0.9
In H_2S	25.2	29.2	19.8	1.5	23.4	21.7	0.0		
Other gases etc	4.0	3.0	12.0	35.8	9.0	7.8			
General Data									
Ash/shale ratio	.668	.657	.672	.666	.663	.665	.799	.906	.935
Kerogen %	33.2	34.3	32.8	33.4	33.7	33.5	20.1	9.4	6.5
Dist. Index	1.47	1.53	0.69	0.68	1.16	1.03	1.17	0.68	0.41
Rate of heating	280	280	80	75	100	100	95	80	85
Oil prodn. time	0.75	0.67	1.5	1.75	2.0	2.0	1.75	1.5	1.0
Max. rate O.P.	109	166	23	29	45	35	29	10	5
Do. per % kero.	3.28	4.83	0.70	0.87	1.33	1.05	1.44	1.12	0.77
Gas production									
Carbon dioxide	75	52	78	62	118	149	n.d.	67	70
H_2S	164	190	129	10	153	135	nil	142	62
Scrubbed gas	1190	1002	3370	3840?	1008	1481	925	186	106
Total gas	1429	1244	3577	3912	1279	1765		395	238
Weight distribn									
Vol. in residue	9.20	11.40	13.10	12.40	11.05	13.00	19.25	35.05	60.00
F.C. in residue	9.00	8.85	14.7	12.00	23.60	17.75	15.80	9.05	0.00
Oil	60.95	63.45	29.85	29.55	46.45	40.60	47.35	27.55	16.90
Water	8.10	6.50	9.00	6.65	7.40	8.00	8.85	13.30	10.30
CO_2	1.25	0.85	1.30	1.00	1.95	2.45		3.95	6.00
H_2S	2.10	2.30	1.65		1.95	1.70		6.40	4.05
Gases etc.	9.40	6.65	30.40	38.40	7.60	16.50	8.75	4.70	2.75
Number of Run	28	29	30	31	32	33	34	35	36

TABULATED DISTILLATION RESULTS

Number of Run	37	38	39	40	41	42	43	44	45
Particle size	¼"	¼"	¼"	¼"	¼"	¼"	¼"	¼"	¼"
Water condensed	3.4	2.2	4.6	5.0	4.6	2.3	2.6	3.0	2.3
Oil Data									
Gallons per ton	45.4	65.0	16.2	16.5	44.0	36.0	22.8	30.0	9.6
Sp. Gr.	.910	.913	.922	.921	.915	.913	.914	.916	.908
Sulphur %	2.53	2.51	2.50	2.50	2.36	2.15	2.28	2.12	2.24
Saturation %	34	32	36	31	31	35	37	30	35
Dist. Analysis									
Below 150 C	12.5%	10.9%	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
150 C - 200 C	11.6	10.5							
200 C - 250 C	10.6	10.7							
250 C - 300 C	13.3	11.8							
Residuum	52.0	56.1							
Residue Data									
Weight in grams	856	767	999		859	914	981	941	1574
% of shale	76.5	68.5	89.15	90.0	76.6	81.5	87.6	84.0	93.7
Prox. Analysis	#/Ø								
Volatiles 900 C	4.8%	4.75	3.5%	4.95	3.6%	5.35	6.3%	6.55	5.1%
Fixed carbon	5.9	4.8	2.8	0.0	5.0	2.2	0.4	1.05	-0.4
Ash	89.3	90.45	93.7	95.05	91.4	92.45	93.3	92.4	95.3
Sulphur	1.74	1.11	1.52	1.66	1.86	1.51	1.85	1.66	1.46
S distribution									
In residue	n.d.	n.d.	50.4	53.0		40.0	57.0	52.3	69.0
In oil			6.0	6.0		10.2	7.5	9.8	4.3
In H_2S			29.2	26.1		34.8	23.4	28.9	28.3
Other gases etc			14.4	14.9		15.0	12.1	9.0	±1.6
General Data									
Ash/shale ratio	.683	.619	.835	.845	.700	.753	.817	.775	.893
Kerogen %	31.7	38.1	16.5	15.5	30.0	24.7	18.3	22.5	10.7
Dist. Index	1.43	1.70	0.98	1.06	1.47	1.45	1.25	1.33	0.90
Rate of heating	80	80	80		70	65	95	100	95
Oil prodn. time	2.5	2.5	2.0		2.0	2.25	1.5	2.0	1.5
Max. rate O.P.	40	62	18		33	28	30	29	16
Do. per % kero.	1.26	1.62	1.09		1.10	1.14	1.64	1.28	1.50
Gas production									
Carbon dioxide	49	48	41	37	75	64	56	54	51
H_2S	274	300	197	185	245	270	167	193	155
Scrubbed gas	950	1085	469	587	951	770	559	752	226
Total gas	1273	1433	707	809	1271	1104	782	999	432
Weight distribn									
Vol. in residue	11.55	8.55	18.90	29.00	9.20	17.65	30.10	24.50	41.10
F.C. in residue	14.20	8.60	15.15	0.00	12.75	7.30	1.90	3.95	
Oil	58.10	69.55	40.10	43.80	59.85	59.35	50.80	54.50	36.40
Water	4.80	2.55	12.45	14.40	6.85	4.15	6.35	5.95	9.60
CO_2	0.85	0.70	1.35	1.30	1.40	1.45	1.70	1.30	2.65
H_2S	3.65	3.35	5.05	5.05	3.45	4.60	3.95	3.60	6.15
Gases etc	6.85	6.70	7.00	6.45	6.50	5.50	5.20	6.20	4.10
Number of Run	37	38	39	40	41	42	43	44	45

TABULATED DISTILLATION RESULTS

Number of Run	46	47	48	49	50	51	52	53	54
Particle size	½"	¼"	¼"	¼"	¼"	¼"	¼"	¼"	-100
Water condensed	2.8	2.4	3.0	5.8	2.2	2.6		6.5	5.0
Oil Data									
Gallons per ton	7.5	46.2	27.6	50.6	29.0	45.9	50.2	41.7	136
Sp. Gr.	.910	.913	.912	.946	.945	.913	.929	.898	.921
Sulphur %	2.36	2.36	2.18	2.36	2.14	2.46	2.34	2.37	2.43
Saturation %	31	30	31	16	18	30	28	44	32
Distillation Analyses of Runs 39 to 60 not determined									
Residue Data									
Weight in grams	1589	863	961	805	948	865	833.5	853.5	159
% of shale	94.5	77.0	85.9	71.8	84.6	77.2	74.4	76.2	35.5
Prox. Analysis									
Volatiles 900 C	6.4	4.55	5.75	3.90	5.70	4.60	5.75	5.40	7.00
Fixed carbon	-1.4	2.40	0.75	3.25	0.20	3.00	4.00	6.40	24.30
Ash	95.0	93.05	93.50	92.85	94.10	92.40	90.25	88.20	68.70
Sulphur	3.15	1.25	1.35	2.09	1.49	1.48	1.88	2.06	2.82
S distribution									
In residue	83.5	42.2%	55.1%	57.7%	61.2%		53.9%	60.4%	25.2%
In oil	2.0	19.5	11.8	19.5	12.6		18.7	15.2	33.8
In H_2S	12.9	37.8	29.5	19.5	22.2		24.9	18.8	40.4
Other gases etc	1.6	0.5	3.6	3.3	4.0		2.5	5.6	0.6
General Data									
Ash/shale ratio	.898	.716	.802	.666	.797	.713	.671	.672	.243
Kerogen %	10.2	28.4	19.8	33.4	20.3	28.7	32.9	32.8	75.7
Dist. Index	0.73	1.62	1.39	1.52	1.43	1.60	1.52	1.27	1.80
Rate of heating	105	105	110	100	100	100	35	0	115
Oil prodn. time	1.5	2.0	1.5	2.5	2.0	1.75	5.0	54	2.0
Max. rate O.P.	10	48	38	46	28	50	20	11.6	140
Do. per % kero	0.98	1.69	1.92	1.38	1.38	1.74	0.61	0.35	1.85
Gas production									
Carbon dioxide	41	64	39	62	16	39	62	56	118
H_2S	116	216	153	127	115	294	163	123	405
Scrubbed gas	195	775	519			812	1250	845	2470
Total gas	352	1055	711			1145	1475	1024	2993
Weight Distribn.									
Vol. in residue	46.35	12.30	24.90	8.40	23.70	12.30	13.00	12.55	3.30
F.C. in residue		6.50	3.25	7.00	0.85	8.10	9.05	14.90	11.40
Oil	29.95	66.30	56.75	64.00	60.00	65.35	63.20	50.75	73.50
Water	12.25	3.75	6.75	7.75	4.80	4.05		8.85	2.95
CO_2	2.05	1.25	1.10	1.00	0.45	0.75	1.05	0.95	0.85
H_2S	4.80	3.20	3.30	1.60	2.35	4.35	2.10	1.60	2.30
Gases etc.	4.60	6.70	3.95	10.25	7.55	5.10	11.60	10.40	5.70
Number of Run	46	47	48	49	50	51	52	53	54

TABULATED DISTILLATION RESULTS

Number of Run	55	56	57	58	59	60
Particle size	-100	⅜"	-100	½"	½"	½"
Water condensed	4.8	2.6	5.2	2.4	6.0	5.4
Oil Data						
Gallons per ton	26.6	43.5	13.5	25.5	49.0	51.6
Sp. Gr.	.915	.919	.911	.912	.947	.940
Sulphur %	2.23	2.36	1.85	2.16	2.38	2.46
Saturation %	32	35	38	37	23	22
Distillation Analyses not determined						
Residue Data						
Weight in grams	951	879	614	968	823.5	819.5
% of shale	84.9	78.5	91.4	86.4	73.5	73.2
Prox. Analysis						
Volatiles 900 C	3.80	5.15	5.50	5.20	5.40	6.00
Fixed carbon	3.35	3.45	1.00	1.70	4.55	3.75
Ash	92.85	91.40	93.50	93.10	90.05	90.25
Sulphur	1.37	1.54	2.15	1.55	1.97	1.93
S distribution						
In residue	68.3%		95.0%	52.55	55.7%	54.3%
In oil	14.1		4.8	8.75	18.9	20.4
In H_2S	15.9		0.0	28.8	22.5	20.85
Other gases etc	1.7		0.2	9.9	2.9	4.45
General Data						
Ash/shale ratio	.789	.717	.855	.804	.662	.661
Kerogen %	21.1	28.3	14.5	19.6	33.8	33.9
Dist. Index	1.26	1.53	0.93	1.30	1.45	1.52
Rate of heating	85	70	65	70	27	60
Oil prodn. time	2.5	2.5	2.5	3.0	5.5	2.5
Max. rate O.P.	23	36	9.2	20	22	44
Do. per % kero.	1.09	1.27	0.63	1.02	0.65	1.30
Gas production						
Carbon dioxide	58	37	45	43	77	42
H_2S	68	272	0	183	147	136
Scrubbed gas	1018	873	490	652		
Total gas	1144	1182	535	878		
Weight distribn						
Vol. in residue	16.30	14.30	34.60	22.95	11.70	12.95
F.C. in residue	12.10	9.55	06.30	7.50	9.90	8.10
Oil	50.95	62.25	37.30	52.55	60.95	63.45
Water	10.15	4.10	15.85	5.45	7.95	7.10
CO_2	1.50	0.70	1.75	1.25	1.25	0.70
H_2S	1.40	4.05	0.00	4.00	1.85	1.70
Gases etc.	7.60	5.05	4.20	6.30	6.40	6.00
Number of Run	55	56	57	58	59	60

DISCUSSION OF RESULTS .

The general data obtained during the 51 distillations performed are reported fully in the preceding pages and it is now possible to trace the influence on distillation of the various factors enumerated at the beginning of this section.

(a) SIZE OF PARTICLE RETORTED.

The average size of particle of the shale being retorted has a definite influence on oil yield and certain other characteristics of the crude oil.

There are two extremes

1. A charge consisting of very fine particles

2. A charge consisting of relatively few but large pieces.

In the former case the oil vapours are brought into intimate contact with the residue from those particles already retorted and at a higher temperature - in most retorting systems heat flow and vapour flow are more or less in opposite directions - and much vapour phase cracking of oil vapour takes place as it passes through a layer of hot residue.

In the latter case although much space exists between the pieces themselves somewhat the same conditions as in the former case prevail as regards each piece where for example the last of the oil vapour has to escape through the outer layers of a lump of residue by now heated much above distillation temperature.

Between these extremes it is possible to have a charge made up of particles of about one quarter inch mininmum dimensions which still allows a reasonable inter-particle porosity and yet no vapour is compelled to traverse more than one eighth inch in order to escape from its parent lump. Under these conditions there is a minimum vapour phase cracking of oil vapour by contact with hot residue. This is clearly shown by considering the distillation indices for runs 15, 21, 22, and 27 as shown in the following tabulation.

Run No.	Minimum dimension of particle	Rate of heating	Max, rate of oil productn.	Distillation Index
27	Less than 1/25"	200 C	70	1.41
21	Less than 1/25"	140 C	65	1.53
15	3/16" - 1/4"	170 C	90	1.57
22	1/2"	175 C	80	1.52

The rates of heating are very nearly alike for the two latter runs whereas for the fine shale one is too high and one is too low. At a rate of heating of 170 C the fine shale would give an intermediate value for the distillation index such as 1.48.

A rate of heating of 170 C per hour is about the upper limit of the optimum rates of heating for shale in quarter inch flakes. For pulverised shale this rate of heating is decidedly above the optimum.

Only four distillations are quoted but they are supported by all the other work e.g. whatever the rate of heating used it is only when particles of ¼" size are used also that the distillation index for the standard sample of shale will reach 1.57. On other samples from different parts of the Latrobe deposit a higher distillation index is found under the same conditions, hence the necessity of working with a standard sample.

At considerably higher rates of heating a different relation is found, a maximum distillation index being reached for a coarser particle than for a lower rate of heating. This maximum is, however, less than for the lower rate of heating. The results of several distillations at rates of heating up to 280 C per hour are given in the following tabulation:-

Run No.	Minimum dimension of particle	Rate of heating	Max. rate of oil productn.	Distillation Index.
27	Less than 1/25"	200 C	70	1.41
28	3/16"	280 C	109	1.47
24	3/16"	260 C	103	1.48
29	1/2"	280 C	166	1.53
25	3/4"	280 C	144	1.52

It was found impossible to distil the finest shale as fast as the coarser sizes and had the fine shale been subjected to more rapid heating the distillation index for this size of particle and 280 C rate of heating would have been still lower.

It will be seen that for very fast distillation - much faster than commercial rates - the efficiency of distillation increases with the particle size up to 1/2" or 3/4" minimum dimension.

The extension of this work to larger particles was prevented by the small size of the retort used but the turning of the curve downwards is rather indicated by the distillation index for Run 25 being somewhat less than for Run 29 whereas an increase in distillation index might have been expected from the trend of the curve up to Run 29.

For the large lumps fed to commercial retorts a very high rate of heating would undoubtedly prove destructive of the oil with reduction of the distillation index as the fine particle conditions hold for the lump considered as an individual charge

and while the minimum dimension of a lump is so great not owing to the laminated nature of the shale, gas and vapour escape is probably easier along the laminations rather than across them.

The high efficiency of distillation obtainable with crushed shale in a suitable retort and under suitable conditions seems to be unattainable under commercial conditions when lump shale is used.

For slow distillation in which the shale takes 5 hours or so to pass through the distillation range the effect of particle size is obliterated by changes in thekerogen and by the vapour phase cracking due to the relatively long contact of residue and oil vapour. Under these conditions the rate of heating or length of time of distillation and the amount of steam used to accelerate flow in the retort and diminish vapour phase cracking are the chief factors determining efficiency of distillation.

(b) RATE OF RISE OF TEMPERATURE OF THE CHARGE.

Data were obtained as regards the variation in distillation index with rate of heating for three different particle sizes. These were

1. Shale crushed through a 20 mesh screen
2. Shale in particles 3/16" - 1/4" minimum dimension
3. Shale in particles 1/2" minimum dimension.

The following tables give the results obtained with the three particle sizes mentioned.

Shale crushed through a 20 mesh screen.

Run No.	Rate of heating	Maximum rate of oil productn.	Total time of oil production	Distillation Index
20	45 C	34	3.5 hours	1.49
21	140 C	65	1.75	1.53
27	200 C	70	1.25	1.41

Shale in particles 3/16" - 1/4" minimum dimension

Run No.	Rate of heating	Maximum rate of oil production	Total time of oil production	Distillation Index
26	10 C	10	12.9 hours	1.27
11	50 C	52	5.0	1.44
10	140 C	72	1.5	1.58
15	170 C	90	1.5	1.57
24	260 C	103	1.25	1.48
28	280 C	109	0.75	1.47

Shale in particles 1/2" minimum dimension

Run No.	Rate of heating	Maximum rate of oil production	Total time of oil production	Distillation Index
19	38 C	26	5.0 hours	1.44
22	175 C	80	1.5	1.52
25	280 C	144	1.0	1.52
29	280 C	166	0.75	1.53

Note. The size of the pieces in Run 25 was fully 3/4" minimum dimension accounting for the slower distillation with the same rate of heating.

It will be seen from theforegoing tables that slow distillation under any condition of particle size always results in a low distillation index. With all particle sizes the efficiency of distillation was increased by using higher rates of heating. With particles of minimum dimensions 1/2" to 3/4" there was no indication of falling off in distillation index even when using heating rates up to 280 deg.C per hour. The maximum efficiency as reflected in the distillation index for the 1/2" sized material falls below that attainable with 1/4" size particles so, that although the distillation index does increase with increased rates of heating, it never for 1/2" material reaches the same value as for 1/4" material under optimum conditions.

With shale particles of 1/4" minimum dimension increasing the rate of heating above a certain optimum rate had the effect of reducing the distillation index so that this figure was at a maximum at a rate of heating of approximately 140 C per hour. Under these conditions any part of the shale is passed through the distillation range in rather less than one hour.

For very fine shale a somewhat lower rate of heating would probably give a higher distillation index but on the other hand for the 1/4" material increasing the rate to 170 C/hour had little effect on the distillation index. By further increasing the rate to 280C/hour the distillation index was appreciably lessened.

The optimum rate of heating thus appears to increase with the particle size.

The work described in Part II of this investigation has shown that prolonged heating at 300 C has the effect of altering the constitution of the kerogen so that it yields a much greater carbonaceous residue on subsequent distillation. In general the faster the shale can be brought up to the distillation range and passed through it the greater the proportion of the kerogen that can be converted into oil. I believe this rearrangement of the kerogen material plays an important part in all cases where the shale takes more than, say, one hour to pass through the distillation range.

Slow distillation is frequently advocated in shale retorting but this present investigation on Tasmanite all goes to show that the slower the distillation the less the oil obtained.

In Run 26 with the temperature rising 10 deg.C per hour and also in the approximately isothermal run No. 53 the temperature throughout the retort was uniform within one or two degrees and the greatly reduced oil yield was not principally due to vapour phase cracking of oil vapour by hot residue etc. but to the fact that part of the oil was not really evolved at all.

In support of this it should be noted that a gram of shale in a closed platinum crucible quickly raised to 900 C will show

a lower fixed carbon calculated as a percentage of the kerogen than will be obtained by igniting to 900 C the retort residue from the most efficient distillation of the same shale.

When the rateof distillation is continually raised by increasing the rate of heating the distillation index does not steadily increase owing to the oil vapours meeting hot retort walls and residue particles and suffering destructive vapour phase cracking. This effect naturally increases with the temperature gradient in the retort and as this is approximately 120 C per inch for the higher rates of heating it is apparent that the last oil coming off passes through residue heated to well over 500 C and a good proportion of it is decomposed.

This effectis more noticeable the finer the shale so that in Run 27 although the rate of heating and maximum rate of oil production were much lowerthan for Run 24 the temperature gradient was 150 C per inch. The vapours were thus more severely cracked resulting in the distillation index being reduced to 1.41.

With coarser shale the opposite holds and in Run 25 although the rate of heating was 280 C as opposed to 200 C for Run 27 the temperature gradient was 75 C per inch or about half that of Run 27. This explains why fast distillation is more suited to coarse rather than to fine shale. However, each large lump behaves very similarly to an aggregate of very fine particles so that however fast the temperature of the outside of the lump is raised the rate of transfer of heat into the lump puts a limit on the speed of distillation. Thus Run 25 with an apparent rate of heating the same as that of Run 29 shows a maximum oil production rate of 144 gallons per ton per hour as against 166 for Run 29. This is solely due to the size of the lump or particle slowing up distillation.

With slow distillation the change in structure of the kerogen extends in an upward direction the oil producing range whereas with fast distillations the oil flow ceases rather sharply when the interior of a fine charge or the interior of the lumps reaches 470 C.

With shale particles not exceeding 1/4" in minimum dimensions there is a minimum of contact of oil vapour and shale residue so that provided the rate of heating is not excessive the retorting of this size shale will give a maximum oil production. No work was done to ascertain whether a charge composed of particles of 1/8" minimum dimension would allow still freer exit of vapours and represent the real optimum particle size. Particles of this size would have to be very free from fines or else the fine shale conditions as in Run 20 etc would hold. With particles of 1/4" size a moderate amount of fines did not seem to affect the results.

As regards the retorting of the relatively large pieces of shale as fed to commercial retorts of the type erected at Latrobe

This work indicates that maximum oil production would be obtained by retorting as fast as possible - the size of the lumps will be the limiting factor - and diminishing the cracking that occurs outside the lumps by suitable use of steam in the retort to accelerate the gas flow. This procedure will, however, show a reduced yield compared with the optimum. The amount of steam that the economics of the question will show the best commercially may be much below the Scothh practice especially if iron retorts are used and purchased fuel has to be used for steam raising. The few percent extra recovery over the practice prevailing at Latrobe in the Crozier retort will not repay much outlay on fuel, steam plant, and extra condensing plant.

A point that has to be borne in mind is that a moderate amount of vapour phase cracking in the retort undoubtedly increases the ease of refining of the lighter fractions of the oil but here again the economics would need careful looking into.

The amount of vapour phase cracking which occurs when the oil vapours are passed over heated shale residue is greatly influenced by the temperature of contact. In the region 450 C to 500 C the action is relatively slow so that if distillation is practically finished by the time the hottest part of the retorted shale reaches 500 C to 525 C the distillation index will be high for the particular grade of shale retorted.

The general influence of temperature on the vapour phase cracking of the oil is more fully discussed in the next section

(c) TIME OF CONTACT OF OIL VAPOURS WITH HEATED RESIDUE AND SURFACES.

In order to gain some information on vapour phase cracking of the oil by contact with shale residue at temperatures from 450 C to 800 C, four experiments were made carrying out distillation and condensation as usual but passing the vapours and gases through a cracking tube maintained at the desired temperature by the tubular elctric furnace shown in the photograph.

The cracking tube was made of 1½" internal diameter iron pipe with one end welded up but carrying a gas union for connection to the retort while the other end was faced plane and closed by a screw cap which also carried a gas union for attachment of the copper tube leading to the condensing assembly. The overall length was 24 inches thus leaving several inches projecting from the 20" long heating furnace.

In the four Runs the retort was heated so that distillation was complete in about 2 hours. The tube was packed as follows

Run 30 370 grams of Residue 19, the oversize on a 20 mesh screen. This occupied 18 inches of the tube and was maintained at approximately 780 C.

Run 31 250 grams of copper turnings occupying 18 inches of the tube and maintained at approximately 675 C.

Run 32 300 grams of residue 23, 20 mesh oversize, occupying 15 inches of the tube and maintained at approximately 460 C.

Run 33 300 grams of residue 31, 20 mesh oversize, occupying 15 inches of the tube and maintained at approximately 560 C.

The results obtained in Run 30 were rather unexpected, approximately 60% of the oil being decomposed and 2400 cu. ft. of gas per ton appearing in its place. Such severe cracking would have little commercial application except in cracking shale oil for gas enriching purposes.

At temperatures approaching 800 C the cracking of this highly unsaturated Tasmanite shale oil is very rapid. Allowing for 50% of the volume of the packed tube being available for gas flow the time of contact in the middle of the distillation is of the order of 2 seconds and this suffices for destruction of fully half of the oil. The inference is obvious that in retort design contact with red hot surfaces is exceedingly destructive of the oil.

In Run 31 copper turnings were used as packing and the cracking tube averaged about 100 C lower than in Run 30. The temperature was maintained more nearly constant. The real object of using the copper turnings was to obtain information as to their action at high temperature on the sulphur compounds in the oil. At the end of the run the turnings were well coated with shiny carbon and probably largely functioned as a carbon packing. In spite of the carbon coating the turnings combined with practically all - 95% - of the sulphur usually evolved as hydrogen sulphide.

The general character of the oil from Run 31 was indistinguishable from that of Run 30, the quantity produced, specific gravity, and saturation all being almost identical the only noteworthy difference being that oil 31 was lower in sulphur which may be explained by the comparative absence of hydrogen sulphide from the gas. On the average 10% of the sulphur content of the crude shale oil is accounted for by dissolved hydrogen sulphide.

There was no appreciable reduction of sulphur content of the oil condensed in Run 31 apart from that explainable by absence of hydrogen sulphide so that it appears that much of the sulphur in Tasmanite shale oil is securely combined as in the heterocyclic compound thiophene and its homologues.

In general there were practically no differences between Runs 30 and 31 except that of temperature. The nett cracking effect in Run 31 was practically the same as in Run 30 in spite of the lower temperature. The higher density and therefore smaller volume packing would allow the vapours a somewhat longer time in the packing tube but on the other hand there was less surface to react on the gas. However the two runs were so much alike that they may be discussed together.

The gas yield is shown to be a little greater in Run 31 but this figure is really 10 to 15% too high owing to a little oil mist wetting the capillary of the flow meter. The gas yield for Run 30 may therefore be accepted as representing both of these runs. The gas was of somewhat higher density compared with ordinary distillation this no doubt being due to the presence in greater quantity of low boiling cracked hydrocarbons not removed by the usual oil scrubbing. Its calorific value would thus be higher than from ordinary distillation.

As regards the oils both showed large petrol and kerosene fractions compared with normal shale oil while the residuum left at 300 C was about half the normal amount. Further than this the residuum was indistinguishable from a coal tar pitch both in smell and in consistency. The lighter fractions of the oil were very distinctly aromatic in character demonstrating again the high thermal stability of the aromatic hydrocarbons

The sulphur content of the crude oil was actually increased by fully 30% of the usual value after allowing for hydrogen sulphide thus indicating that the heterocyclic sulphur compounds characteristic ~~shale~~ of this shale oil share the thermal stability of the aromatic series. The sulphur compounds are decidedly more stable than the paraffins under these cracking conditions since the crude oil showed little or no increase in saturation compared with normal distillation.

In Run 32 the temperature of the cracking tube was too low by 20 to 30 C to avoid condensation and retention of the heaviest fractions of the shale oil. The oil actually collected was 39 gallons per ton or almost exactly 75% of the highest yield obtainable from the same shale. It is only fair to say that judging from the proximate analysis of the cracking tube residue probably up to 7 more gallons of oil per ton may have been obtained by allowing the cracking tube to heat up at the end of the run. This, however, is not beyond question.

The crude oil obtained in this run - 32 - is remarkably similar to that from the very slow distillation, Run 26, in specific gravity, sulphur content, and saturation. Distillation of heavy oil from the cracking tube would raise the former and lower the two latter. However there is general similarity and thus the effect of very slow distillation with the shale taking 12 hours to pass through the distillation range can be obtained in one sixth the time by vapour phase cracking even at the moderate temperature of 460 C.

A further run with vapour phase cracking was then carried out at a higher temperature, the actual cracking tube temperature averaging very closely 557 C.

In Run 33 the residue used in the cracking tube was retort residue from Run 31 and had the fines screened out by a 20 mesh sieve. The experience gained in theprevious three runs enabled the cracking tube to be kept very constant in temperature so that for the two hours that the oil was coming over the greatest variation in the cracking tube temperature from the mean of 557 C was 3 C and usually it was much less than this.

In every way this run was very satisfactory. Taking 52.5 gallons as the maximum yield of the shale, only 65% of this was recovered. The pressure necessary to drive the vapours through the cracking tube appears to produce more retort cracking than usual. This effect plus the deposition of carbon in the cracking tube and generation of more gas produces a comparatively low oil yield.

The characteristics of the oil, low specific gravity and relatively high saruration are typical of a considerably cracked shale oil. The oil, however, was distinctly a shale oil in

contrast to oils 30 and 31. The sulphur content 2.52% of which 0.35% is removable by washing with sodium hydroxide is not by any means low so that vapour phase cracking of this type offers no easy solution of the desulphurising problem.

The oil contained nearly one fourth of its volume boiling below 150 C and thus was rich in the petrol fraction as well as in thekerosene fractions. The residuum left at 300 C was similar to ordinary shale residuum in being quite fluid at room temperature while that from Runs 30 and 31 was definitely solid having the consistency of a soft pitch. Owing to the comparative absence of paraffins ordinary shale residuum left at 300 C flows readily at the freezing point of water.

These vapour phase cracking experiments all show that the carbonaceous shale residue is very active in decomposing the easily decomposable shale oils even at 550 C. At higher temperatures the action is much more rapid. For maximum oil production in retorting it is clearly necessary to avoid contact of theoil vapours with hot shale residue as far as possible and to keep the vapours away from very hot retort walls etc.

The effect of severe vapour phase cracking at 700 C - 800 C on the oil is to largely increase the amount of aromatic hydrocarbons at the expense of the unsaturateds and the paraffins but this effect is not prominent at a lower temperature such as 550 C. At this latter temperature the paraffins seem relatively stable whereas the unsaturated hydrocarbons are rapidly decomposed thus increasing the paraffin content. Gum-forming hydrocarbons such as the diolefines are relatively easily decomposed so that a moderately cracked oil yields light distillates which can be freed from gum-forming compounds with less acid treatment than necessary in the case of normally distilled shale oil.

Any retorting variation which diminishes the contact of oil vapour and residue e.g. the use of steam in retorting, produces a crude oil very highly unsaturated and the light distillates from such a crude oil are undoubtedly harder to refine than the more cracked oil obtained in the absence of steam.

A moderate amount of vapour phase cracking in the retort may be economic as a greater proportion of the more valuable lighter oils is produced and refining costs would be less. If, however, cracking was practised on the bulk of the crude oil - excluding tops and bitumen - it would probably be better to aim at a maximum oil production even if more unsaturated crude oil was obtained.

(d) EFFECT OF STEAM, CARBON DIOXIDE, HYDROGEN ETC. DURING DISTILLATION.

It is frequently advocated that retorting in a stream of permanent gas will give desirable results and while this is partially true as regards the separation of the oil from the residue, great difficulties are introduced as regards the condensation of the oil. By using steam the advantages of accelerated flow in theretort are reaped but condensation is not seriously interfered with apart from having to condense the steam with its high latent heat.

The use of incombustible gases such as carbon dioxide or flue gas possesses the further disadvantage of spoiling the retort gas for heating purposes. However, for the sake of completeness the effect of retorting in a current of carbon dioxide was investigated.

One distillation was also made in a current of hydrogen to ascertain the specific effect of hydrogen.

Three distillations were carried out using a steam flow through the retort and as the first of these appeared somewhat unsatisfactory as regards steam flow, a repeat distillation was made with more regular steam flow and thus Run 14 may be accepted with greater weight than Run 13. At a much later date Run 52 was made at a much lower rate of heating and using approximately the amount of steam used in the Scotch retorting practice. It will be convenient to consider distillation in steam first.

In Run 14 distillation was carried out with a rate of heating which was subsequently found to be the optimum for the size of shale used. The amount of steam used was equivalent to 40 gallons of water per ton of shale distributed evenly throughout the distillation. In Run 13, 40 gallons was also used but the steam flow was irregular, being small during the middle of the distillation thus accounting for the smaller percentage of the kerogen recovered as oil in Run 13.

Steam equivalent to 40 gallons of water was used to carry over 52 gallons of oil and accompanying gas. The average rate of flow in the retort would be increased sixfold by the use of this quantity of steam owing to its low molecular weight and thus the time in which vapour phase cracking could take place is reduced to one sixth. This is apart from any specific action of the steam on the decomposition of the kerogen or on the oil vapours. The presence of steam in the retort appears to favour, if anything, the leaving of a little more carbonaceous matter in the residue compared with simple

distillation at the same rate of heating e.g. in Runs 13, 14, and 15 the percentages of kerogen left in the residue were 20.85, 20.20, and 19.25 respectively. In Run 15 the centre of the charge was heated to 546 C compared with 533 in Run 14 and this would leave somewhat less carbonaceous matter in the residue heated to the highest temperature but does not to my mind account for the difference.

The presence of steam thus does not seem to have any favourable influence on the cracking of the pyrobitumen into oil but the accelerated flow in the retort greatly reduces the vapour phase cracking.

Run 14 considered from thepoint of view of fraction of kerogen converted into oil is distinctly the most efficient distillation conducted on the standard sample, 66.25% of the kerogen appearing as oil as against 64.9% in Run 15 and 65.5% in Run 10. The result for Run 15 deserves greater weight for comparative purposes. The small increase in efficiency when using steam is undoubtedly due to the diminution of vapour phase cracking in the retort so that oil is obtained instead of gas to some extent. Of course, a higher grade shale will show a greater fraction of the kerogen converted into oil by simple distillation e.g. Run 38 where the fraction converted is 69.5%.

The efficiency of steam distillation does not appear in the distillation index to its full credit as oil distilled with a full steam flow has a specific gravity exceeding 0.950 from this sample of shale whereas under conditions for maximum oil production without use of steam 0.926 is an average figure.

The oil from steam distillation is rather poor in the lower boiling fractions as would be expected from its specific gravity and the figure of 11% over at 150 C in the 100 m.l. distillation analysis would probably reduce to 9% on large scale distillation. This applies to the first fraction in all cases and especially where the quantity of light fraction is small as the lag of the thermometer behind the temperature of the vapour makes more difference than often recognised. On large batches of oil there is often up to 2% less of the lightest fraction recovered compared with the 100 m.l. distillation.

The saturation of the steam distilled oil is only 14% and the separation of this quantity of saturated hydrocarbons is only obtained on continued centrifuging. The sulphur content of the steam distilled oil was 2.60% which is relatively high for Tasmanite shale oil especially as it would be somewhat lower in hydrogen sulphide owing to the nature of the distillation. It would appear that with the use of steam the only advantage is that a little greater weight of oil is recovered.

Against this it is certain that the oil would present some additional refining difficulties.

The use of steam to diminish vapour phase cracking in the retort does not show up to full advantage in laboratory distillation at rates of heating near the optimum. In fast distillation in a small laboratory retort the vapour phase cracking is not excessive as the rapid evolution of gas and oil vapours maintains a rapid flow in the retort and consequently the opportunity for vapour phase cracking is fairly small. At lower rates of heating much more vapour phase cracking takes place.

In Run 52 a distillation was made in steam using a rate of heating in the distillation range of 35 C/hour which is near a commercial figure and accelerating flow by using 77 gallons of water as steam per ton of shale. This amount of steaming is approximately that used in the Pumpherston retort. With this quantity of steam the volume occupied is a little more than 10 times the volume of permanent gases actually produced in this run and nearly 8 times the volume of gas plus oil vapour on the assumption that the average molecular weight is about 200.

The steam flow was very uniform compared with the time and would not therefore be in a constant ratio to the oil vapour and gas as the flow of these rises to a maximum and then falls off. The partial pressure of products of retorting would average only 12% of the total pressure in theretort and the condensible oil vapours themselves instead of composing about 40% of the total gases and vapours in the retort would be nearer 5% of the total. Vapour phase cracking under these conditions should be reduced to a small magnitude, say under one gallon per ton on the standard sample.

The actual oil recovery was 50.2 gallons per ton instead of 47 - 48 which would have been obtained in the absence of steam and as against 52 gallons under optimum conditions - the ash content was slightly higher than usual in the standard sample.

It will thus be seen that ample steam flow prevents the destruction of 2 - 3 gallons of oil per ton in slow distillation. The discrepancy in oil yield between slow distillation at 35 C per hour rate of heating and fast distillation at 140 C - 170 C per hour rate of heating is accounted for to the extent of 60% or thereabouts by vapour phase cracking in the retort while the remainder is due to constitutional changes in the kerogen produced during the slower heating.

The general character of the oils produced in Runs 14, 19, and 52 are as follows

	Run 14	Run 19	Run 52
Specific Gravity	0.952	0.903	0.929
Saturation	14%	36%	28%
Sulphur %	2.60	2.19	2.34

It will be noticed that the degree of saturation of the oil seems to be more influenced by the length of time of the distillation rather than by the reduction of vapour phase cracking.

For slow retorting the use of steam to accelerate flow in the retort is a decided advantage resulting in the recovery of 5% more oil and possibly still more under certain bad retorting conditions. The Scotch retorting practice of using much steam is thus seen to be sound in regard to the retorting of Tasmanite if oil yield alone is the primary consideration.

Distillation in hydrogen

In the run in which hydrogen was used to accelerate flow the amount of this gas used was not very much greater in volume than the total volume of retort gas plus oil vapour. The oil vapours would therefore travel through the retort in something less than half of the time necessary in the absence of the hydrogen. The vapour phase cracking in the retort would thus be diminished but not as much as in steam distillation.

The general results of this distillation compare very closely indeed with those of Run 15 which is a check run under similar conditions excepting the hydrogen flow. Superficially it would appear that the hydrogen had little influence on distillation but this is hardly the case. In the hydrogen the amount of kerogen appearing in the residue is 17.75% whereas in Run 15 it is 19.25. The hydrogen thus seems to have a small specific action in causing more volatile matter to be evolved though the increased difficulties of condensing the low boiling oils by reason of the reduction of their partial pressure by dilution with hydrogen prevented the recovery of the additional oil. The oil scrubber catch was 8 m.l. or 1.6 galls/ton and it seems probable that nearly this quantity of spirit escaped in the gas owing to the increased gas volume. The rather low -150 C fraction in the distillation analysis confirms this view.

The sulphur content of the crude oil was 2.31% . This would be somewhat lower than normal on account of being in equilibrium with a gas lower in hydrogen sulphide by reason of the dilution with hydrogen.

In general it seems that distillation in a current of hydrogen approximately equal in volume to the retort gas produced has no noticeable influence on the sulphur content of the oil or on its saturation. A small specific action on the kerogen seems to be indicated which at higher pressures would probably be much increased. As an aid to ordinary atmospheric retorting the use of hydrogen would seem to be of no advantage whatever.

Distillation in carbon dioxide

Retorting in carbon dioxide is not likely to be of any interest commercially but in view of the adverse action of carbon dioxide in some English experiments on oil shales reported in the "Industrial Chemist and Chemical Manufacturer" it is of scientific interest.

The volume of carbon dioxide used in Run 12 would be approximately 1.5 times the volume of retort gas and oil products so that the vapour phase cracking in theretort would be diminished in proportion. In spite of this the fraction of kerogen appearing in the residue is somewhat greater than for ordinary distillation suggesting a slight adverse action of the carbon dioxide on the production of oil from the kerogen. The fraction of the kerogen recovered as oil was 63% but this figure was adversely affected by the poor spirit scrubbing of the mixed gas. Only one scrubber was used and 2.4 gallons/ton of spirit recovered in it. If additional scrubbers had been used, it is probable in the light of later experience that an additional one to two gallons of spirit pr ton would have been recovered bringing the total yield nearly to 52 gallons. The actual recovered oil yield in Run 12 thus shows distillation in carbon dioxide in a rather unfavourable light.

It is considered that the adverse influence of carbon dioxide on oil yield is, if any, small but the difficulties of condensation are increased in proportion to the increase in the amount of permanent gas leaving the retort. Any method of retorting in which the oil vapours mix with the products of combustion or are carried over in a stream of incombustible gas is thus handicapped by greatly increased condensation difficulties and also by the incombustibility of the retort gas rendering it useless for heating purposes.

(e) EFFECT OF OTHER SOLID SUBSTANCES IN THE CHARGE.

Several years ago it was freely reported that the addition of limestone to the charge was beneficial and this was the reason for carrying out Run 17. In Run 17, 10% of pulverised Ida Bay limestone, 96% $CaCO_3$, was mixed with the charge.

There were no indications of any advantages gained by this procedure. The sulphur content and saturation of the oil produced were quite normal. There were indications of a little more retort cracking indicated by 20.9% of the kerogen appearing in the residue and by a somewhat larger than usual percentage of -150 C fraction in the crude oil. The oil yield was only 50 gallons per ton making the distillation index 1.49. This charge and that of Run 18 was coarser than for previous runs and the influence of particle size was not then fully appreciated. The coarser particle size would itself reduce the distillation index a little but the lower results are considered in the main to be due to the presence in the charge of extra surface thus increasing the vapour phase cracking in the retort.

In general the presence of inert material in the retort appears undesirable from the point of view of oil yield in that it increases the vapor phase cracking of the oil. It may thus increase the proportions of the lighter fractions as claimed at the time in question but the same result can be obtained in cheaper ways.

In Run 18, 10% of freshly burnt quicklime was used as an addition to a charge somewhat coarser than for Runs 10 to 16. No influence of the lime was noticed beyond a slight increase in theretort cracking and the very definite holding back as calcium-sulphur compounds of about 75% of the sulphur usually evolved as hydrogen sulphide. The crude oil was a little lower in sulphur than usual as it contained less hydrogen sulphide.

It would again appear that the addition of inert material to the charge is unsound and that the use of quicklime in particular has no appreciable effect in producing oils of lower sulphur content from Tasmanite.

(f) THICKNESS OF CHARGE IN THE RETORT.

The influence of the thickness of the charge or the distance to which the heat must penetrate from the wall of the retort is intimately bound up with the relative directions of heat and vapour flow.

In many retorts these tend to right angle and counter flow and in these cases the thickness of the charge becomes very important. From the point of view of maximum yield the ideal retorting arrangement would have the directions of heat and vapour flow alike and in this way contact of oil vapours with red hot shale residue with its destructive cracking effect would be avoided. In addition from the work described in PART II the subjection of shale to hot oil vapours would appaer to have an advantageous effect on the kerogen in producing more oil.

In the types of retort with different directions of heat and vapour flow, the thermal gradient which must necessarily exist in any retort in order to transfer heat to the centre becomes of paramount importance.

The thermal gradient in degrees Centigrade per inch plotted against rates of heating in the neighbourhood of 350 C yields for crushed shale - mostly in flakes 3/16" to 1/4" in thickness - an approximately straight line for all rates of heating up to 4 degrees Centigrade per minute. The latter represents the limit of the heating furnace used. The points naturally vary a little owing to small variations in the size of particle but the slope of the curve averages 18 C per inch per 1 C per minute rate of heating. Thus in Run 16 with a rate of heating of approximately 3 degrees per minute in the early part of the distillation the thermal gradient was 52 C per inch. In Run 21 in which the same rate of heating was used but the charge was -20 mesh the thermal gradient was approximately doubled being actually 107 C per inch. This was borne out in the other two cases where -20 charge was used, the thermal gradient being a little over double that for the coarser size mentioned at the same rate of heating. For still coarser shale i.e. in lumps 3/4" - 1" in the smallest dimension and 2 -2½" in the largest, the thermal gradient was reduced to 14 C per inch per 1 C per minute rate of heating.

In commercial retorting larger pieces are used but in addition a fair quantity of fines are necessarily included so the temperature gradient to be expected on the richer shale is of the order of 15 C per inch per 1 C per minute rate of heating. The coarser the shale the lower the temperature

gradient as the spaces allow convection of heat by gases in an increased degree.

By consideration of these figures it will be seen that in order to raise the interior of a charge to 480 C or 500 C to complete the distillation, the rate of heating in a retort in which the heat has to penetrate say 10 inches would have to be fairly low if the wall temperature of the retort is to be kept down to a safe figure for iron retorts.

If the flow of the vapours is different from that of the heat then the thickness of the charge exercises a large influence on account of the vapour phase cracking that takes place. This is seen magnified in fast retorting of fine shale as in Run 27. Here the last vapours were compelled to come into intimate contact with only 1⅛" of hot residue but owing to the high temperature gradient the cracking of the later oil that came off must have been severe as the charge was considerably coked together and the oil yield was 10% under the optimum.

On large scale retorting while the temperature gradient may be much smaller the total temperature difference between the exterior and the centre of the charge may be as great or greater than in Run 27 quoted above and as the vapours flow towards and along theretort wall the total vapour phase cracking in the absence of steam may be much greater resulting in much loss of oil and unwanted carbonisation trouble.

In one instance that came under notice a shale yielding 46 gallons per ton under optimum conditions of distillation yielded about 29 gallons in an overheated commercial retort. Part of the discrepancy is attributable to lack of spirit scrubbing but the recoverable spirit would not be more than three or four gallons per ton even allowing for the greater amount of spirit produced by the vapour phase cracking.

It seems obvious that retorts must be designed to secure heat penetration without running to too high a wall temperature if iron retorts are to be used and excessive vapour phase cracking avoided.

(g) MAXIMUM TEMPERATURE OF DISTILLATION NECESSARY.

During the course of this work it has been clearly shown that if the shale is heated fairly rapidly distillation is complete when the coolest part of the charge reaches 470 C or at most 480 C. If distillation has been carried out very slowly the attainment of 500 C may be necessary in order to expel the last traces of oil.

Distillation may be carried out at lower temperatures e.g. Run 53 in which the temperature averaged approximately 410 C and after sufficient time at this temperature, say, 60 to 80 hours no further oil would be evolved on raising the temperature. In such a case only about 75% of the optimum yield is obtained. In all ordinary distillation work in order to complete the expulsion of the oil about 480 C may be looked on as the upper limit of the distillation range.

The Capertee Valley shale of N.S.W. which is of a different type requires a temperature slightly in excess of 505 C in order to complete distillation.

The problem is to raise the whole of the charge to at least the necessary temperature without injury to the retort. In those retorts which have a brick lower section such as the Pumpherston no difficulty arises. It is, however, possible to retort Tasmanite without undue difficulty in a properly designed cast iron retort provided iron of suitable composition is used for its construction. There is not much margin between the wall temperature that must be attained in order to complete retorting and the temperature at which the life of the iron castings is appreciably shortened so that retort failures have not been infrequent in the past.

It is improbable that the ammonia yield of the shale will become commercially important and this being so cast iron retorts should be able to stand up to the conditions imposed on them when oil alone is the object of distillation.

(h) PRESSURE UNDER WHICH RETORTING TAKES PLACE.

The influence of the absolute pressure of retorting is intimately bound up with the principles discussed in sections (c) and (d). Retorting under reduced pressure is very similar to retorting in a current of permanent gas and unless the retort gas is compressed back to atmospheric pressure the condensation of the lighter fractions and the scrubbing of the lower boiling hydrocarbons out of the gas is just as difficult.

Owing to lack of apparatus in the first two reduced pressure distillations made, the gas could not be brought up to atmospheric pressure before spirit scrubbing so that condensation was adversely affected. In the second two reduced pressure runs an attempt was made with a receiver to catch the retort gas and thus bring it up to atmospheric pressure. This was moderately successful but owing to an inaccessible air leak in the system the full benefit of this refinement was not gained.

Four low pressure distillations were thus made:-

1. Standard sample, 66.6% ash, and rate of heating 100 C per hour. Run 49.

2. Shale sample, 79.7% ash, and rate of heating 100 C per hour. Run 50.

3. Standard sample, 66.2% ash, and rate of heating 27 C per hour. Run 59.

4. Standard sample, 66.1% ash and rate of heating 60 C per hour. Run 60.

In the first case the pressure in the condensing system was lowered by a water pump and averaged 11 c.m. of mercury at the delivery pipe from the retort while most of the oil was coming off though at the end it decreased to 7 c.m. The pressure in the retort would be approximately one seventh of an atmosphere and the vapours would remain in the retort only one seventh of the corresponding time under normal distillation.

The results showed that the fraction of the kerogen remaining in the residue was only 15.4% which is decidedly the lowest of any distillation on this grade of shale. This is reflected in the residue weighing only 71.8% of the weight of the shale charge instead of 72.9% which is the figure for normal pressure. The finishing temperature was, however, higher than usual and thus

partly accounts for the lesser amount of kerogen left in the residue.

The actual collection of oil was only 50.6 gallons though it was of high specific gravity and accounted for 64% of the weight of the kerogen. The oil scrubber catches totalled 0.6 gall. only while if the gas could have been scrubbed at atmospheric pressure this would have apparently nearer to 4 gallons and the total oil yield would have been nearer to 54 gallons corresponding to a distillation index of 1.60.

It would appear that distillation at reduced pressure is the most succesful method of converting the greatest fraction of the kerogen into oil and gas and while the use of sufficient steam in the retort will decrease the contact of oil vapour and shale residue to the same extent, reduced pressure retorting appears to give the best results. By comparing Runs 14 and 49 on the same grade of shale, in the steam run it will be seen that 20.2% of the kerogen remained in the residue whereas in the case of the reduced pressure run 15.4% remained. Actually there would be somewhat less vapour phase cracking in Run 14 as it was a faster distillation so that it seems reasonable to conclude that the steam has actaully a slight adverse effect on the cracking of the pyrobitumen into oil and gas by causing more of the kerogen to remain in the residue.

In the case of Runs 48 and 50 which were atmospheric and reduced pressure runs respectively on the same grade of shale - the same sample was used for both - the reduced pressure run was decidedly more efficient as regards the percentage of the kerogen left in the residue, the figures being 28.1% and 24.5%.

There was also a difference in ash content of 0.5% and in the direction to make the reduced pressure run the more efficient. The actual collection of oil was greater in the reduced pressure run in spite of the poor spirit scrubbing that accompanies working at reduced pressure. It seems in this case that either reduced pressure has a greater effect in the case of lower grade shale or that some other factor was operating. The former view seems the more probable.

The distribution of sulphur in the various products of distillation is distinctly altered by retorting at low pressure as may be seen from the tables on the next page.

RICHER SHALE ASH 66.5% APPROX.

	Atmosph.Press		Reduced Pressure Runs			Steam
	Run 15	Run 19	Run 49	Run 59	Run 60	Run 52
Rate of heating Deg.C per hour	170	35	100	27	60	35
Sulphur distribution						
Residue	46.3	48.2	57.7	55.7	54.3	53.9
Oil	19.9	16.8	19.5	18.9	20.4	18.7
Hydrogen sulphide	30.8	29.4	19.5	22.5	20.85	24.9
Other gases etc.	3.8	5.6	3.3	2.9	4.45	2.5
Percentage of kerogen in residue	19.25	23.15	15.4	21.6	21.05	22.05

POORER SHALE ASH 80% APPROX.

	Atmospheric Pressure	Reduced Pressure
	Run 48	Run 50
Rate of heating Deg.C per hour	110	100
Sulphur distribution		
Residue	55.1	61.2
Oil	11.8	12.6
Hydrogen sulphide	29.5	22.2
Other gases etc.	3.6	4.0
Percentage of kerogen in residue	28.1	24.5

The effect of reduced pressure in the case of both shales is to decrease the amount of sulphur evolved as hydrogen sulphide and to increase that left in the residue. The oil is not appreciably altered in sulphur content. It therefore appears that the rapid removal of the vapours either decreases the secondary action of the various hydrocarbons on inorganic sulphur compounds or alters the mechanism of the cracking of the pyrobitumen which has been shown to contain nearly 6% sulphur. The former supposition seems very probable but it is possible to distil the part of the shale in powder form containing all the pyrite without any disengagement of hydrogen sulphide.

In this case the oil contained very nearly the normal amount of sulphur.

In any case the production of hydrogen sulphide seems to be of a secondary character to some extent for decrease of contact of evolved gases and decomposing kerogen decreases the amount formed. This is so even when the partial pressure of the hydrocarbons is reduced by dilution with steam.

In all low pressure runs the specific gravity of the crude oil was increased as some of the more volatile part was uncondensed. The raising of the specific gravity was, however, principally due to diminution of vapour phase retort cracking as in the steam runs. This is borne out by the fact that the saturation percentage of the crude oil from the richer shale was reduced to 16% or nearly the same as in a fast steam run. With the richer shale and slower distillation more saturated oils were produced again showing that speed of distillation is the principal factor controlling the saturation and that vapour phase cracking is only of secondary importance in this regard. The crude oil from the poorer shale dropped from 31% saturation to 18% by using the lower pressure.

The pressure under which retorting takes place seems to have a considerable influence on the proportion of kerogen which remains in the residue. The preceding discussion has made it clear that the lower the pressure the smaller the proportion left in the residue. Increasing the pressure has the opposite effect. Although not specifically investigated light is thrown on this question by those runs in which the vapours were passed through a cracking tube and the retort thus subjected to some increase of pressure which, however, was not determined.

The average fraction of the kerogen left in the ~~cracking tube~~ retort residue (excluding deposition in the cracking tube) in Runs 30, 31, 32, and 33 is approximately 24% compared with 19.25% for distillation at atmospheric pressure and 15.4% at low pressure, all on the same grade of shale.

The effect of pressure thus seems very definitely to have a destructive effect on the oil and although a quantitative investigation would have been desirable it was held over owing to shortage of time.

The constant volume experiments detailed in PART I had also shown the destructive effects of pressure retorting and consequently it was not thought worth investigation compared with the pressing problems involved in investigating oil composition and refining.

(11 VARIABLE EFFICIENCY OF CONVERSION OF KEROGEN TO OIL WITH VARYING RICHNESS OF SHALE.

The distillation of a few shale samples showed a notable variation of distillation index with varying richness of shale so that it was determined to investigate this point more thoroughly when the opportunity presented itself.

The opportunity came when the Committee appointed to investigate the local shale industry decided in April 1931 to carry out a systematic sampling of the available shale exposures.

Selected samples from this survey covered the range from 65% ash to 90% ash and these were retorted under conditions which would produce the maximum amount of oil, i.e. using shale particles of about 1/4" minimum dimension and approximately 100 C per hour rate of heating. Some of the lower grade samples were rather too fine as they pulverise very readily and much fine material had been produced in the sampling crushing. The rates of heating were a shade on the low side in some cases owing to the heavy winter heating load on the College mains.

The specific gravities of most of the samples were determined and are included in the table of data. These specific gravities were determined on the pulverised shale by the bottle method using kerosene oil or alcohol as the fluid medium as the small amount of oil present in the raw shale precludes the use of water except with considerable difficulty and with increased liability to error. A few specific gravities were determined as checks using water and boiling off the entrained air under the vapour pressure of water at about 25 C. These results checked those obtained with oil and since the use of oil was much less troublesome it was used for the majority.

The grade of the shale or its yield on distillation is very closely related to the specific gravity and a careful determination of the specific gravity in the case of the average sample will give the oil yield to within 2 gallons per ton. The specific gravity of ignited shale ash is usually about 2.70.

In the table on the next page is given in order the serial number of the run, description of sample, ash percentage on the shale dried at 100 C, specific gravity. oil yield in gallons per ton, kerogen percentage, distillation index, and percentage of the kerogen recovered as oil.

T indicates top seam, M.B. middle band, B bottom seam. Runs 54 and 55 are the float concentrate and residue respectively from a 1.32 sp. gr. ferrous chloride separation. Run 57 is the residue from a carbon tetrachloride separation of pulverised shale. 58 is a composite whole seam sample and 34 is of unknown source from the Australian Sale Corporation lease.

RUN NO.	SAMPLE	ASH %	SP.GR.	OIL YIELD	KEROGEN	DIST.IND.	OIL/KERO %
54		24.3	1.7	136	75.7	1.80	73.5
38	T.	61.9	1.71	65.0	38.1	1.70	69.55
15	T.	66.5	1.87	52.6	33.5	1.57	64.9
37	T.	68.3	1.90	45.4	31.7	1.43	58.1
41	T.	70.0	1.94	44.0	30.0	1.47	59.85
51	T.	71.3		45.9	28.7	1.60	65.35
47	T.	71.6	1.94	46.2	28.4	1.63	66.3
56	T.	71.7		43.5	28.3	1.53	62.25
42	B.	75.3	2.04	36.0	24.7	1.45	59.35
44	B.	77.5	2.12	30.0	22.5	1.33	54.5
55		78.9		26.6	21.1	1.26	50.95
34	?	79.9	2.14	23.6	20.1	1.17	47.35
48	B.	80.2	2.17	27.4	19.8	1.38	56.75
58	W.S.	80.4		25.5	19.6	1.30	52.55
43	B.	81.7	2.25	22.8	18.3	1.25	50.8
39	B.	83.5	2.24	16.2	16.5	0.98	40.1
40A	M.B.	84.5	2.29	16.5	15.5	1.06	43.8
57		85.5		13.5	14.5	0.93	37.3
45	M.B.	89.3	2.48	9.6	10.7	0.90	36.4
46	M.B.	89.8	2.56	7.5	10.2	0.73	29.95
35	M.B.	91.1	2.48	6.4	8.9	0.72	27.55
36	M.B.	93.5	2.65	2.7	6.5	0.41	16.9

In the accompanying graph the distillation index, the oil yield, and the conversion efficiency of the kerogen are plotted against ash content or reading from the right hand end of the graph kerogen percentage.

The only shales available are included between the limits 61.9% ash and 93.5% ash. Many of the samples were representatively taken across the particular seam but the details of the history of a few is obscure except that the mine or lease they came from is known. As no richer shale than 61.9% ash could be obtained a rich concentrate was made by floating pulverised shale in a ferrous chloride solution of 1.32 specific gravity.

It will be seen that the two efficiency relations, the distillation index and the conversion efficiency of the kerogen, have a pronounced curvature although some of the points fall on either side of the curves. The oil yield curve on the other hand is practically a straight line intersecting the ash or kerogen axis at 94% ash or 6% kerogen. It is drawn straight though it might reasonably have been flattened a little to take in the last four points.

With such a composite material as oil shale close mathematical relations could hardly be expected to connect the oil yield with ash content but eliminating the results on those samples the low results of which can be qualified e.g. Runs 55 and 57 were on 200 mesh powder and would give low results, and Run 34 was on a very unusual sample of shale - the oil yield under conditions approaching the optimum is a straight line function of part of the kerogen.

A shale of 95% ash would apparently produce no oil on distillation. It was not possible to verify this point as it is very seldom that the ash content of the middle band rises even to 92% on a sample taken right across the band. For practical purposes on the known part of the field samples of over 91% ash are so rare as to be not worthy of consideration. It is thus sufficiently accurate to draw a straight line intersecting the ash axis at 94%.

Approximately 6% of the weight of all shales examined can be looked on as ineffective in the production of oil although this portion of the shale is largely of an organic nature. Even on distillation, and in passing it should be noted that some water is produced during the later stages of distillation, seldom more than 2 - 3% of the weight of the shale is obtained as watery liquor. Mineral combined water will not account for very much but it is significant that in certain runs which produced more oil than would be expected from the general relationship e.g. Runs 38, 51, and 47 the amount of water produced was smaller than usual.

In these cases the oil producing material may have been less hydoxylated which would give a higher than usual distillation index.

If then the ashless portion of the dried shale is termed kerogen and this is reduced by 6% (on the shale) the remaining effective kerogen produces oil in a constant ratio independent of the grade of the shale. The factor or distillation index for this effective kerogen is about 1.92 so that except for the poorer middle band samples which seem to produce a gallon or so more oil per ton than this straight line function would indicate, the oil yield under optimum conditions can be found fairly closely by deducting ash plus 6% from 100 and multiplying the remainder by 1.92.

For example take the standard sample, ash content	66.5%
Apparent kerogen	33.5%
Effective kerogen	27.5%
Calculated oil yield in gallons per ton of dry shale	53

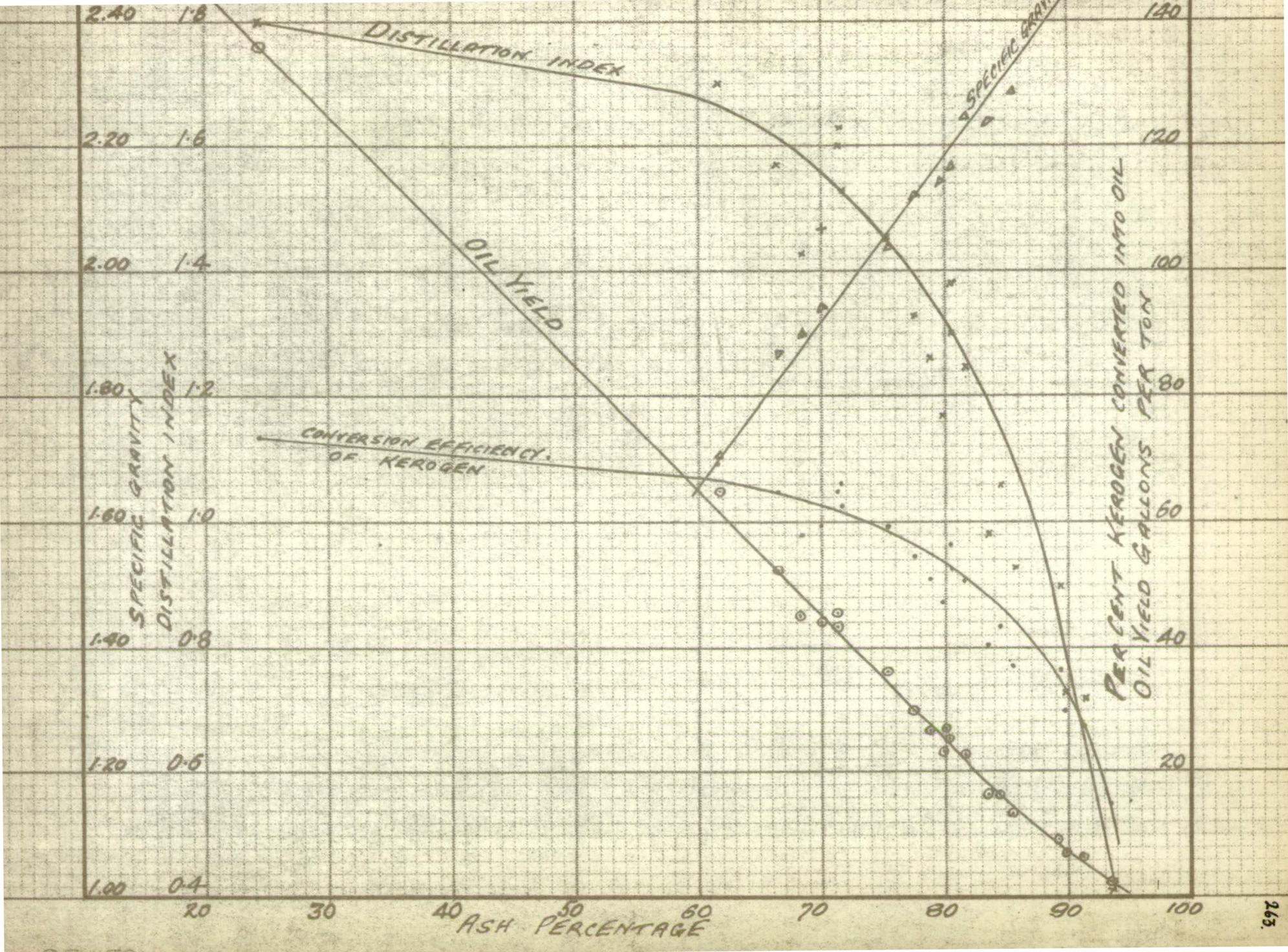
For a poorer shale ash content	89.3%
Apparent kerogen	10.7%
Effective kerogen	4.7%
Calculated oil yield in gallons per ton of dry shale	9

The poorer shales are thus poorer than they appear from the ash content owing to the ineffective portion of the kerogen increasing in relative importance with increase of ash till a point is reached at which no oil is produced.

If on the other hand the kerogen is considered as a whole there is a marked falling off in the efficiency of conversion of kerogen into oil which is indicated by the rapid drop in the two efficiency curves when the ash exceeds about 70%.

These figures are based on a very small laboratory retort but nevertheless a retort and heating system which could be kept under close control. With commercial retorts these yields are impossible of attainment and 85 to 90% of these maximum or optimum yields is all that can be obtained on the usual grades of shale. The reasons for this discrepancy are given in the section dealing with the correlation of the yields in the Crozier retort with those obtained in this laboratory.

In general if the grade of the shale is judged on a simple ashless basis as denoted by the broad term kerogen, the efficiency of the conversion of kerogen into oil is more largely determined by the richness of the shale than by any other single factor yet studied. This factor seems to have escaped notice hitherto as far as can be ascertained from the literature. Its great importance cannot be overlooked when commercial production of oil from Tasmanite oil shale is being considered.


DISTILLATION INDEX
OIL YIELD
SPECIFIC GRAVITY
CONVERSION EFFICIENCY OF KEROGEN
SPECIFIC GRAVITY
DISTILLATION INDEX
PER CENT KEROGEN CONVERTED TO OIL
OIL YIELD GALLONS PER TON
ASH PERCENTAGE
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
140
120
100
80
60
40
20
20
30
40
50
60
70
80
90
100

GENERAL OBSERVATIONS ON RETORTING.

From consideration of the foregoing experimental work it transpires that the conditions necessary for the production of the maximum yield of oil from a moderately rich Tasmanite shale and possibly from all grades of Tasmanite oil shale are as follows.

1. Shale in particles whose minimum dimension does not exceed one quarter inch. Fine dust should preferably be at a minimum.

2. Rate of heating in the distillation range 100 C to 150 C per hour.

3. The temperature of the shale should be raised to the distillation range as quickly as possible. A rate of heating of 150 C per hour is sufficiently high.

4. Heat and vapour flow should be parallel.

5. The surfaces with which the evolved vapours come in contact should not be over 500 C and better results will be obtained if they are not over 450 C.

6. Steam is not required if conditions 2, 3, and 4 are fulfilled. Steaming will increase somewhat the oil yield by weight but not by volume.

It does not necessarily follow that the above conditions are the ideal ones to be adopted on a commercial scale. The accumulated experience would seem to indicate otherwise as the retorting of lump shale with minimum dimensions of the lumps often exceeding 2" is general practice. Too much crushing with the resultant production of fines introduces too much resistance to vapour and gas flow and there is the danger of a complete blockage of a vertical retort by fine material.

In commercial retorting rates of heating fall much below those given above but all indications point to as fast a distillation as possible compatible with keeping the retort walls at a safe temperature. One of the greatest disadvantages of a low heating rate is that the oil producing material undergoes constitutional change resulting in the production of less oil on subsequent distillation.

Heat and vapour flow are parallel in the N-T-U internal combustion retort and this from a technical point of view redeems this retort which is somewhat crude in its operation though possibly with improvement this retorting system may ultimately on sufficiently rich shales prove a commercial success.

In most retorts vapour flow is partly toward the wall though mainly at right angles to the heat flow which is inwards from the wall. In the Crozier retort with its multiple off-takes the directions of vapour flow are very diverse but both in this retort and in the Pumpherston retort the current of oil vapour comes in contact with the hot retort walls and hot shale residue already distilled. In the Pumpherston system of retorting much gas is made in the lower brick section and this gas together with the steam admitted very much reduces the contact of oil vapour and hot retort wall.

With the present knowledge of Tasmanite shale retorting it would seem that usual commercial retorting without steam will not give much more than 80% of the assay value of the shale but by using sufficient steam to distribute heat and to diminish vapour phase cracking in the retort recoveries of over 90% would be possible. Attainment of laboratory maximum yields which are obtained at comparatively high rates of heating is impossible in nearly all commercial retorts as with the relatively low rates of heating used in these the evolution of the maximum quantity of oil is prevented.

CORRELATION OF CROZIER RETORT OPERATION WITH LABORATORY DISTILLATION.

Some amount of work was carried out on several samples to determine the relation of the yield in the Crozier retort to that of the laboratory retort.

The Crozier retort was run under closely uniform conditions of feed for periods of the order of two weeks or more, and samples of the feed taken regularly. These were mixed and then cut down to a suitable size for retorting in the laboratory retort. About six samples were received, but time did not allow of more than three being distilled,

The following are the relevant data:-

Test Run No. 2. March 1932.

Period of steady running 14 days.
Average daily throughput 9.75 tons.
Oil produced 34.3 galls. per ton.
Specific Gravity of oil 0.941
Oil left in Residue 1.1 gallon per ton.

Laboratory result. Run 51.

Oil produced 45.9 gallons per ton,
Specific Gravity of oil 0.913.

	Volume basis,	Weight basis.
Commercial recovery	74.8%	77.0%
Left in Residue	2.4%	2.5%
Cracked to gas and carbon etc.		20.5%

Test Run No. 3. May 1932. Shale from old workings band excluded.

Period of steady running 14 days,
Average daily throughput 11.7 tons.
Oil produced 35.1 gallons per ton
Oil left in residue 0.5 " " "
Specific gravity of oil 0.934

Laboratory Results, Run 56

Oil produced 43.5 gallons per ton
Specific Gravity of oil 0.919

	Volume basis.	Weight basis.
Commercial recovery	80.7%	82.0%
Left in Residue	1.1%	1.1%
Cracked to gas and carbon		16.9%

Test Run No. 3A, June 1932. Whole seam sample of shale from new workings (band excluded).

Period of steady running	15 days
Average daily throughput	12.6 tons
Oil produced	22.7 gallons per ton
Left in residue	nil
Specific gravity of oil	0.934

Laboratory results

Oil produced	25.5 gallons per ton
Specific Gravity of oil	0.912

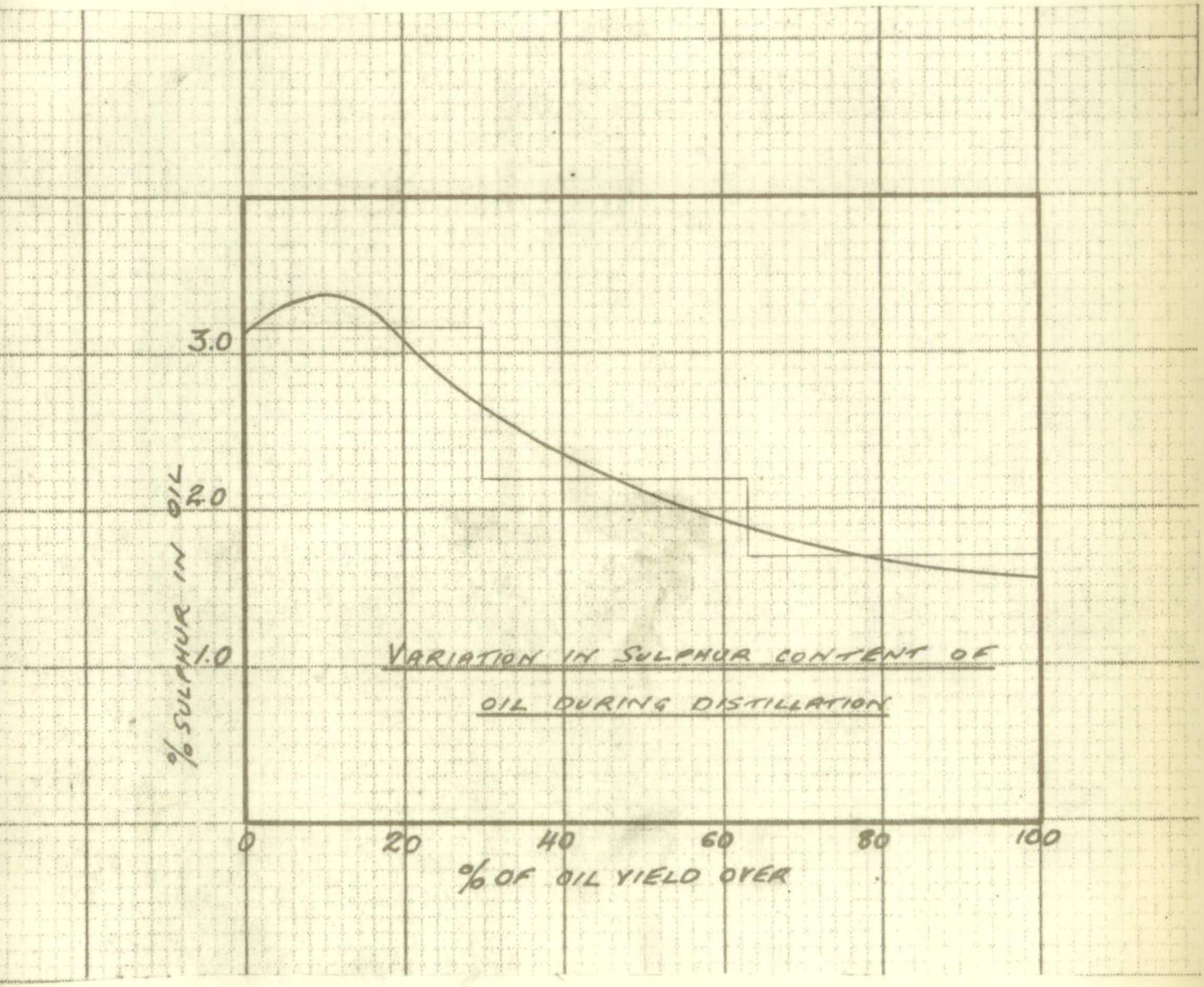
	Volume basis.	Weight basis
Commercial recovery	89%	91%
Left in residue	nil	nil
Cracked to gas and carbon etc.		9%

In Test Run 3A, the laboratory sample retorted at Latrobe gave a slightly higher result, bringing the commercial yield on a weight basis to somewhat under 90%. There is no doubt that the retort yields were being steadily improved during these test runs, part of the improvement being due to changes in the heating flues designed to give quicker heating in the early stages of retorting,

A fourth test run, 3B, for 12 days on shale from the new tunnel (as in test run 3A) but with the middle band excluded and with a daily throughput of 11.6 tons gave an extraction compared with the Latrobe laboratory assay of 88%.

It seems reasonable to infer from the above figures that the Crozier retort operated with comparatively little steam will give an extraction of 85% of the laboratory yield as determined under conditions producing the maximum yield of oil. The discrepancy compared with the maximum laboratory figure is chiefly made up of vapour phase cracking loss producing a greater quantity of retort gas and fixed carbon in the residue compared with laboratory conditions. Oil left in the residue only accounts for a small portion of the discrepancy. A Crozier retort operated with a full steam flow, as in the Pumpherston retort, should produce 90% of the assay value of the shale without difficulty.

No opportunity presented itself to correlate the operation of the Pumpherston retort with the laboratory work.



VARIATION IN SULPHUR CONTENT OF OIL DURING DISTILLATION

VARIATION IN THE COMPOSITION OF THE CRUDE OIL AS DISTILLATION PROCEEDS.

From time to time retorting systems are advanced embodying "fractional eduction", as it has been called, or, in other words, it is assumed that the light oils distil first and the boiling point of the distillate rises continuously to the end of retorting. On these premises it is claimed that by having suitable off-takes from the retort a separation can be made from the outset of the various fractions of oil.

In order to test this out and to gain an idea of the progressive change in the nature of the crude oil produced, a slow distillation was carried out on fine shale with a rate of heating of 45°C., and the crude oil was collected in three approximately equal parts. Distillation analysis on 50 c.c., specific gravity, and sulphur content were obtained for each part.

It will be seen by reference to the result sheet for Run 20 that the specific gravity shows a progressive rise, corresponding to the decrease in the amount of lower boiling fractions. It will be seen also that the "fractional eduction" idea is partly borne out by the test but, in general, it is nothing like complete.

The sulphur content of the oil undergoes a progressive change, as may be inferred by setting out in graph form the amounts of sulphur contained in each fraction and drawing a smooth curve through the average values for each fraction. This curve would then indicate that the oil at the commencement contains about 3.7% of sulphur (including hydrogen sulphide). The form of the curve is apparently not as simple as this, as a sulphur determination on the first drippings of oil at 350°C. ran out at 3.15% S. It is clear, however, that the first oil produced is higher in sulphur than average, and there is a gradual drop in the sulphur content as distillation proceeds. The explanation is that in the higher homologues the sulphur atom ø is relatively less important on a weight basis.

TOTAL AMMONIA YIELD FROM THE SHALE.

The ammonia yield was determined in Runs 10, 11, 13, and 14, and was found to be of a low order - approximately 1 lb of ammonium sulphate per ton in ordinary distillation, and somewhat more when using steam. Determination of the nitrogen by the Kjeldahl method gave about 0.25% nitrogen with an indistinct end point. This is equivalent to a little over

26 lbs. per ton of ammonium sulphate for complete conversion to ammonia. Not all the nitrogen would be in a form to produce ammonia, so, to determine the yield on heavy steaming and by high temperature, two separate runs were made on a charge of 224 grams of standard sample.

Experiment I. Distilled shale rapidly in 20 minutes and then raised to 1000°C. passing a continuous current of steam.
Ammonium sulphate yield 8.8 lbs./ton.

Experiment II. Distilled shale and raised to 950°C. Held at 950°C. and passed steam through for 1½ hours. Carbon nearly burnt right out by action of steam. Steam used approximately 225 galls. water /ton. Ammonium sulphate yield 8.45 lbs./ton.

It will be seen that the two experiments are a good check on each other and, further, that the amount of ammonium sulphate recoverable from the shale is comparatively low and below a commercial amount in these days of low ammonia prices. Later work has shown that the spore case material runs about 0.64% N, while the kerogen in the sample used for these two experiments would run a similar % of nitrogen. As this sample is a rich shale, it is reasonable to suppose that the poorer shales with less kerogen material content would yield a correspondingly less amount of ammonia on distillation, As the average of the present known exposures is near to 25% Kerogen, probably the average ammonia content of the shale recoverable by steaming could be placed at 5-6 lbs.am.sulphate per ton.

As a source of ammonia, Tasmanite is thus much inferior to Scotch shale,

The distribution of the nitrogen content of the shale among the various products has been studied in this particular case of steam distillation for maximum ammonia recovery.

Taking the sample to consist, as reported in Part IV, of spore case material 21.4% and remaining material 78.6%, the nitrogen content of the shale works out as follows:-

21.4%	@ 0.64% nitrogen	=	0.137
78.6%	@ 0.155%	=	0.122
	Total nitrogen content		0.26 %

This figure is slightly higher than the direct assay, but the difference is not great.

Nitrogen recovery expressed as a percentage of the shale.

Oil 51 gallons per ton .952 sp. gr. and .27% N	=	.058
Ammonium sulphate 8.6 lbs./ton average yield	=	.081
Left in Residue and evolved as gases		.12 %

It is seen that about 22% of the nitrogen in this sample of shale is found in the oil, while 31% is convertible to ammonia. Approximately half remains with the residue or is evolved as gas.

According to "Shale Oil" by R. H. McKee, A.C.S. Monograph No. 25 p. 117, Scotch shale yields

as ammonia	17.0%	of total nitrogen
Oil - basic tars	20.4	" "
Residual coke	62.6	" "

but when distilled very slowly these figures are respectively 32.8%, 20.0% and 47.2%.

On page 103 of the same author, Scotch shales are stated to yield 65% of their nitrogen content as ammonia when commercially distilled. No work on Tasmanite shale has been carried out on a commercial scale to determine the ammonia yield in the pumpherston retort, although a retort of this type has been operated for a short time.

PART IV.

DISTRIBUTION OF SULPHUR IN THE STANDARD SAMPLE OF SHALE.

The several forms in which the sulphur is present in the shale is a matter of more than passing interest.

The method used by Harding and Thordardsen[*] in determining the amount of sulphate and sulphide sulphur in Colorado shale was tried with the following results.

Sulphate Sulphur.

5 grams treated with 2.9% HCl for 40 hours at 60° C. in a thermostat.

Results: weight of $BaSo_4$			
	Blank	.0007	
	No. 1	.1679	= .46%
	2	.1640	= .45%

Sulphide Sulphur + Sulphate Sulphur.

1 gram treated with cold 1:3 nitric acid for 72 hours.

Results: weight of $Ba\ So_4$			
	Blank	.0024	
	No. 1	.1024	= 1.37%
	2	.1015	= 1.36%

Giving Sulphur as sulphates		.45%
" sulphide		.91%
" organic sulphur		1.24%
Total		2.60%

On this showing somewhat less than half of the sulphur was in combination in the Kerogen.

Further work on the same sample was carried out by grinding the shale through a 100 mesh screen and floating off a concentrate in carbon tetrachloride. The spore case material is thus freed practically completely from the bulk of the gangue and the material

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[*] Forms of Sulphur in Colorado Shale - Journal of Industrial and Engineering Chemistry, Vol. 18, 1926, p. 731.

which sinks in carbon tetrachloride appears to contain no spore case fragments. Purification of the float concentrate by means of hydrofluoric acid, etc. is described more fully in Part V.

The standard sample of shale was found to consist of three principal portions,

Pure ash-free spore case material	21.4%
Another type of organic matter	11.8%
Ash	66.8%

The non-mineral portion of this sample of shale is very approximately two-thirds spore cases and one-third of the other type of material. Both are oil yielding but the former much more so.

The proportion of sulphur present in the shale as spore case material is therefore

21.4% of spore case material at 4.70% = 1.01%

leaving 0.23% S associated with the remaining 11.8% of the shale. This material still runs therefore nearly 2.0% sulphur.

In this particular sample of shale, then, the sulphur distribution may therefore be expressed as follows:-

Spore case material 21.4% of shale accounts for	1.01 %
Remaining organic matter 11.8% of shale	0.23 %
Sulphur present as pyrite, etc.	0.91 %
Sulphur present as sulphates	0.45 %
Total	2.60 %

It will be noted that the sulphur combined in the spore case material represents 38.8% of the sulphur content of the sample while the sulphur in the remaining organic matter is approximately 8.9% of the total sulphur content. Sulphide sulphur then accounts for 35.0% and the remaining 17.3% is present as sulphates.

The water soluble sulphate content of many samples of shale was determined in the Mines Department laboratory at Launceston, and the various samples showed considerable variation both in the amount of water soluble sulphates and in that the proportions combined with calcium and magnesium, the two principal bases, were different in different samples.

The water soluble salts were extracted from 128 grams of finely pulverised standard sample by repeated washings, but the rate of solution was very slow and it is possible that weak hydrochloric acid would have dissolved more sulphate. This is indicated by the water soluble sulphate sulphur falling appreciably below that found in the 60° C. treatment with hydrochloric acid. The general magnitude is, however, in satisfactory agreement.

The water extract from this sample of shale was very low in potash and chlorides and these were not quantitatively determined, but ferrous iron, magnesium, calcium sulphate and phosphate were accurately determined. The 128 grams yielded in milliequivalents

	Basic	Acid
Ferrous iron	0.20	
Calcium	19.05	
Magnesium	7.45	
Sulphate radicle		26.90
Phosphate radicle		0.19
	26.70	27.09

The sulphur present in .0269 equivalent of sulphate is .43 gram or .34% of the shale sample. The water soluble sulphate sulphur is thus approximately 75% of that yielded on acid extraction.

In distillation the sulphate and sulphide sulphur are unaffected and the sulphur in the oil produced is derived from the organic sulphur.

This is in agreement with the distillation results on samples taken from different portions of the field. Samples high in pyrite but low in spore cases yield somewhat lower sulphur oils owing partly to a lesser production of dissolved hydrogen sulphide and partly to a diminished sulphur content apart from the hydrogen sulphide. On the other hand, samples of the richest shales high in spore case material give oils somewhat higher in sulphur.

Although not investigated in an extensive way, it appears that all the organic matter present in the shale contains sulphur, but only the spore cases yield primary hydrogen sulphide on destructive distillation. The other type of organic matter yields no primary hydrogen sulphide on distillation but at the same time yields an oil nearly as high in sulphur content as the spore case oil.

It is, of course, by no means certain that 4.70% represents the upper limit of sulphur content of the spore cases, though in the few samples examined from the Tasmanite shale oil Company's property there was uniformity in this respect. One sample from the other side of the river, and mined in the Australian Shale Corporation's time, yielded spore cases of 1.38% S only. These spore cases were different from the usual and normal type and appeared burnt or affected by igneous intrusion. The percentage of spore cases present in the same shale was also low, viz. 2.5% of ash-free material.

No normal spore cases so far examined have shown a sulphur content differing from 4.7%, but this cannot be taken as evidence that the sulphur

content is invariable. However, it is felt that the spore case material has a closely constant composition as all samples of spore cases are very similar, except near igneous contacts.

The proportion of spore case material in different samples is quite variable, and this, coupled with the variability in the sulphate and sulphide contents, makes the sulphur distribution very variable for different samples. As, however, the sulphate and sulphide sulphur content is unaffected by distillation to temperatures of 500°C. and as the spore case material yields the bulk of the oil in most samples, the sulphur content of the oil, apart from dissolved hydrogen sulphide, is comparatively constant and independent of the pyrite content of the shale. This constancy of sulphur content has been well borne out in the examination of the oils produced from the survey samples.

PART V.

NATURE AND COMPOSITION OF THE OIL YIELDING MATERIALS OF TASMANITE.

Mr. P. B. Nye, M.Sc., B.M.E., Government Geologist, Tasmania, brought under my notice a paper* in German giving the results of certain work on a sample of Tasmanite oil shale by several investigators in Switzerland.

In this paper, which is chiefly concerned with a palaeo-botanical study of fossil sporopollenins, is described a method for the separation of the spore cases from tasmanite. Unbroken spore cases were preferred so that the method of separation involved treating a coarser and a finer portion. Excluding this refinement which seemed somewhat useless in this case, the method of separation was as follows:-

1. Removal of water soluble salts from the shale powder.
2. Treating the dried washed shale with carbon tetrachloride.
3. Treatment of the crude float concentrate with hydrofluoric acid to dissolve silica, etc.
4. Washed with hydrofluoric acid followed by concentrated hydrochloric acid and then water.
5. Boiled repeatedly with 10% potassium hydroxide solution till the liquor remained colourless.
6. Washed by decantation with warm soap solution to remove fine mineral matter such as clay, if any.
7. Extracted in succession with alcohol, ether, carbon disulphide and pyridine.
8. Washed with glacial acetic acid followed by hot water.

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* Helvetica Chimica Acta, Vol. XIV, 1930.

9. Digested with cuprammonium hydroxide for removal of filter paper fibres.

10. Filtered and washed with 24% ammonium hydroxide, then with dilute hydrochloric acid and finally water.

11. Extracted with alcohol, then ether and finally dried in vacuo at 100° C.

It must be admitted that the spore cases possess unusual chemical resistance to emerge unscathed after such a series of treatments, but it appears that, with the exception of concentrated sulphuric acid and concentrated nitric acid, they are unaffected by nearly all other reagents.

In the article the statement is made that the spore cases are free from nitrogen and sulphur and a formula is given for the material of the Tasmanite spore cases or Tasmanin, which has no nitrogen or sulphur in the molecule. On reading this statement interest was aroused, as, if it were true, the separation of the spore case material and its conversion into oil might solve the larger part of the pressing refining problems. The indications of past experience were that the sulphur and nitrogen contents of the shale were very intimately associated with the oil producing substance or substances, so that, in view of the rather revolutionary nature of this new view, it was thought advisable to check up the work on samples that were known to be representative. Supposing that the analytical work in the paper quoted above was beyond suspicion and that the spore cases obtained were really nitrogen and sulphur free, two doubts arise. The first of these concerns the nature of the sample used by the Swiss investigators, the sample used by them may not have been a normal one, and the second doubt arises out of the drastic purification treatment of the spore cases.

It was accordingly decided to repeat the Swiss work on samples that were representative, and particularly on the standard sample upon which so much other work had already been done.

Separation of spore cases.

In order to gain experience of the technique, a variety of shale known at Latrobe as "soft shale" was first used. The sample had been supplied some time previously by Mr. Anderson of the Tasmanite Shale Oil Company and was from that mine.

The general method of separation outlined above was followed except that dilute hydrochloric acid was used to extract soluble salts in step 1. The washed and dried shale was then screened through 120 mesh following the original article but as both coarse and fine portions gave a float with carbon tetrachloride both floats and both residues were combined. The screening is valuable if complete spore cases are desired, but screening after the whole purification process is

is ended is just as effective. The method of separation was then followed to the end of step 6 and the spore cases were dried off at this stage.

The first separation on these lines was carried out on 24 grams of soft shale, and yielded

Spore case concentrate 6.48 grams of 25.0% ash
Spore case free residue 17.0 grams of 84.0% ash

Assuming that the 25% ash in the spore cases is combined with organic matter etc., as in the spore free residue, there was 70.2% of pure spore cases in the concentrate. Taking 6.28 grams of spore concentrate - .2 gm. was taken for ash - there should be approximately 4.4 grams of pure spore cases present.

After purification, the dried spore cases weighed 4.04 g. and contained approximately 0.8% ash. The ash-free spore case material present therefore in the float concentrate (allowing for the ash determination sample) is 4.15 grams or 17.3%.

This sample of shale ran 66% ash so that on this separation the 34% of non-mineral matter is only about half accounted for by spore case material.

A repeat of this work on 100 grams of soft shale which had not been so finely ground as the preceding sample gave in general confirmatory results. After extraction of the water soluble and drying and screening through 120 mesh, the portions obtained were

+ 120 45.5 g. - 120 53.0 grams.

The latter gave a mere trace of float with carbon tetrachloride so that it was not further proceeded with. The former on separation gave

Float 27 grams. Residue 18 grams of 68.6% ash.

The latter was not finely enough ground to separate all the spore case material and assuming that the spore case free residue ran 86% ash there was still 18.2% of pure spore cases present, or 3.3 g.

Purification of the 27.0 grams was carried on to stage 6 and then a carbon tetrachloride float given to remove sand grains and any wax picked up from the waxed vessels used. The spore cases weighed 15.8 grams and still had 1.2% ash, giving slightly over 15.6 of ash-free spore cases. The total quantity of ash-free spore cases would be approximately 18.9%

The two separations approximately check one another and it may be accepted that the spore case content of the sample of soft shale does not exceed about 19% of the dried shale. There was approximately 34% of non-mineral matter in this sample of soft-shale, so that the organic matter is by no means composed of spore cases only.

Purification of the spore cases below about 1% of ash was not attempted. The colour of the ash was the usual light pink, indicating that the mineral matter still associated with the spore cases contained little pyrite.

The nitrogen content of the spore cases was determined by the Kjeldahl method and proved to be 0.64%. Blank determinations were run at the same time and were deducted, though of practically negligible magnitude. The sulphur content was accurately determined and was found to be 4.66% on the sample, or 4.70% sulphur on an ashless basis. These results are at variance with the Swiss work, but are in accord with the work described in Part II, where the pyro bitumen formed from the spore cases assays 5.6% sulphur.

Work on standard sample of shale.

A pilot test on 128 grams of standard sample proved that the compact and tough shale was amenable to the same treatment, though this was somewhat more difficult. The purified spore cases contained 1% of ash and as part at least could be seen by polarised light to be enclosed in the spore cases, which when cleaned look like flattened grape skins, no attempt was made to reduce the ash below this figure. These spore cases also contained 4.70% of sulphur on an ashless basis.

The specific gravity of the spore cases of this degree of purity was determined by suspending in various mixtures of carbon disulphide, carbon tetrachloride and petrol. It was found that practically all sinks in a fluid of 1.08 specific gravity and practically all floats in fluid of 1.12 specific gravity.

In Dana's Mineralogy the composition of Tasmanin is given as

C	79.34%
H	10.41
O	4.93
S	5.32

and the specific gravity as 1.18. This specific gravity could not be confirmed and the analysis given above appears deficient as no nitrogen is mentioned. It is very likely that the sample referred to above contained ash and the analysis is calculated to an ashless basis.

The specific gravity would seem to lie in the range 1.08-1.12. As this is a fairly low specific gravity, attempts were made to separate the spore material in saturated sodium chloride solution and in solutions of sulphuric acid of varying concentrations.

For this purpose a portion of standard sample of 66% ash was put through 100 mesh with the exception of some spore case material which was put through 80 mesh.

The dry weight was 621 grams.

Sodium chloride brine of 1.21 sp. gr. was first tried but the solution would not wet the slightly oily shale particles very completely and separation was poor. The same applies to sulphuric acid of 1.6 specific gravity. However, in 1.3 specific gravity sulphuric acid a good separation was obtained provided the solution to solids ratio was kept about 7 to 1. From the concentrate 16% of the shale was recovered as purified spore case material of 0.95% ash, but some spore case material still remained with the residue as this ran 79.9% ash.

As a reasonable separation of the pulverised shale into a spore case rich concentrate and a poor residue was shown to be possible, it was decided to separate sufficient concentrate for a distillation charge.

After preliminary tests, a ferrous chloride solution of 1.32 specific gravity which was available was used in place of sulphuric acid. The crude float was refloated twice in clean liquor to further separate fine residue. The residue from the main separation was also refloated in clean liquor but gave no further float. The combined residues and the float were washed free of iron salts, dried, and weighed.

The total quantity of shale used was 2488 grams and it contained 0.8% moisture. It had been pulverised by mechanical pulveriser through 100 mesh and most of it was much finer than this.

The general figures are as follows:-

		Ash content open dish	Prox analysis
Dry shale used 2488 x 99.2 =	2468 grams	67.95%	66.8 %
Dry float	526 "	23.6%	23.25%
Dry Residue	1855 "	79.9%	79.2 %
Loss by solution and handling	87 "		

Ash Balance on separation - ash by open dish ignition.

Float	526	at 23.6	124 g.	Shale	2468	at 67.95	1678 g.
Residue	1855	at 79.9	1482				
Loss by solution etc.			72				
			1678 g.				1678 g.

Ash Balance on separation - ash by proximate analysis.

Float	526	at 23.25	122 g.	Shale	2468	at 66.8	1648
Residue	1855	at 79.2	1469				
Loss by solution etc.			57				
			1648				1648

The ash balances are included to give a general idea of the degree of care used in the work. The standard sample lost 1.72% of its weight on water extraction. This would account for approximately 42 g. of the 87 deficiency in the recovered products. Figure (42). This is not very different from the ash loss obtained in the ash balance based on the proximate analysis. There were, however, some minor handling losses such as are difficult to avoid when handling this quantity of material. It is also probable that the ferrous chloride solution might dissolve more material from the shale than water alone. There is also an oily material in the raw shale amounting to approximately 1% by weight and the removal of this wholly or in part would add to the handling loss without affecting the ash balance. It is fairly certain that some at least of this material was removed as the ferrous chloride solution wetted the shale fairly readily.

The concentrate as obtained is still contaminated with much mineral matter, viz. 23.25%. Assuming that this mineral matter is associated with organic matter in the proportion 86 : 14, the concentrate consists of pure ash-free spore cases 27.1% and spore case free residue 72.9%.

The residue was not free from spore material and on treatment with CCl_4 gave a float concentrate of 10.7% of spore case material of 23.4% ash.

The residue from the carbon tetrachloride separation ran 87.3% ash by open ignition as against 87.2 in previous tests.

The ash obtained in the proximate analysis was 86.0%. Assuming that spore case free residue in this sample* runs 86.0% ash (p.a.), the residue 79.2% ash (p.a.) consists of 92.1% spore free residue and 7.9% spore case material.

Assuming that the ash in the spore case concentrate obtained by treating the main residue with carbon tetrachloride is all associated with organic matter in proportion of 86 : 14, there is 27.2% of spore free residue in the carbon tetrachloride concentrate and 72.8% of ash free spore cases.

This 72.8 x 10.7 gives 7.8% of ash free spore cases in the residue from the ferrous chloride separation. These two ways of calculation are in very satisfactory agreement.

This sample of shale would appear to have been resolved by the ferrous chloride separation into

Concentrate	526 grams	27.1 %	spore free residue.
		72.9 %	spore case material.
Residue	1855	92.2 %	spore free residue.
		7.8 %	spore case material.

The sample would consist of

Spore cases in concentrate	383.5 g.
" " in residue	145
Total	528.5 g.

Residual matter free from spore cases

in concentrate	142.5
in residue	1710
Total	1852.5

Loss in separation - mostly by solution of soluble salts etc. 87 g.

The oil yields in distillation of the two species of oil producing matter can be determined from the simultaneous equation given below. Let x = oil yield of spore case material in gallons per ton
y = oil yield of spore case free residual material.
Then

Run 54 $72.9\,x + 27.1\,y = 136$, whence
Run 55 $7.8\,x + 92.2\,y = 26.6$ $x = 181.7$, $y = 13.5$.

The ash as found by calculation from the weight of retort residue and its ash for the samples distilled in Runs 54, 55, and 57 is slightly different from the values used in the preceding calculations and upon which the simultaneous equation is based.

They are compared below

	Direct determination.	Calculation from Residue
Run 54	23.25 % ash	24.3 % ash
55	79.2 % "	78.9 % "
57	86.0 % "	85.5 % "

There is a possibility that in Run 54 retort scale was removed with the strongly adherent residue and the ash was thus increased. These calculated ashes give a somewhat different constitution of the shale, but the difference is not very great. The effect of the higher ash on the rich material is to attach a higher oil yield to the spore cases. The actual oil yields obtained by working the equation out on this different basis are

Spore cases	184.5 galls. per ton
Spore case free residue	13.4 galls. per ton.

The rates of heating during distillation were 115° C. and 65° C. per hour respectively.

It is to be regretted that the separation was not cleaner than it was, but some gallons of carbon tetrachloride would have been necessary. It would not have been possible to get the material used in R 54 any cleaner with CCl_4, as with carbon tetrachloride a lesser proportion of spore case material is obtained in the crude concentrate. The residue, however, would have been free from spore case material.

The general results then are that floatation of the pulverised shale in 1.32 specific gravity ferrous chloride solution separates it into two fractions, one rich in spore case material and one poor in the same material. By distilling these separately and obtaining the oil yield, it has been possible to compute that the spore case material on distillation in the pulverised form yields 182 gallons of oil per ton, and that the spore case free residue also yields oil, but only at about 13.5 gallons per ton in the powder form.

Very good confirmation of the correctness of this view was obtained in Run 57, when a charge of 672 grams of spore case free residue prepared by separation of the spore cases with carbon tetrachloride was distilled and yielded 13.5 gallons per ton. All these figures are on fine charge - 100 and though comparable among themselves are not quite comparable with results on other sizes of shale.

If the small error due to the removal of soluble matter from the shale is ignored, then it is possible to calculate the oil yield of pulverised shale of this type from its constituent parts. Take Run 21 in which the charge was -20 mesh and the rate of heating 140°C. 66.5% of ash corresponds to 77.4% spore free residue and 22.6% spore cases. The oil yield will be approximately

22.6 %	of	182	41.1
77.4 %	of	13.5	10.4
			51.5 galls./ton.

The actual yield was 51.5 galls./ton.

For Run 20, where the shale was 66.0 ash, this is equivalent to approximately 76.8 of spore case free residue and 23.3% of spore cases. The oil yield will be

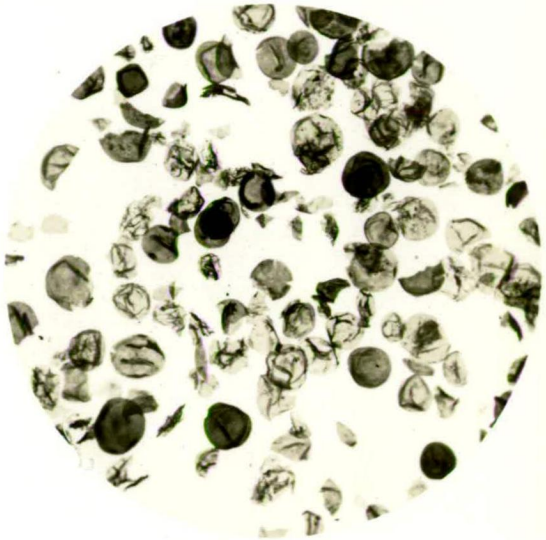
23.2 %	of	182	42.2
76.8 %	of	13.5	10.4
			52.6 galls./ton.

The actual yield was 50.6 galls./ton, but as the rate of heating was on the low side and distillation somewhat prolonged, the yield would have been somewhat larger for faster distillation.

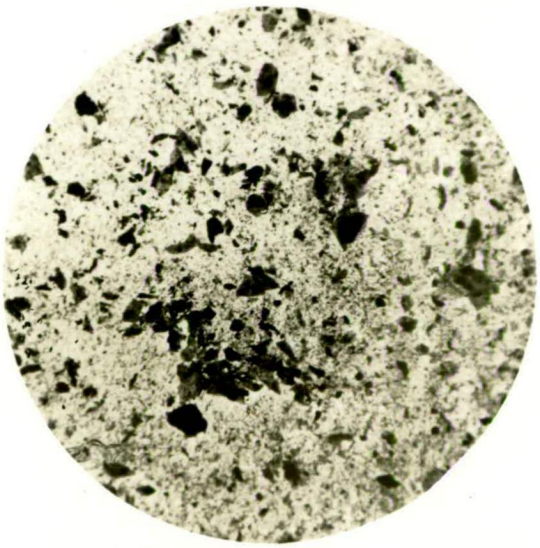
However, averaging the two cases, the oil yield in pulverised form can be computed fairly closely from the oil yields of the constituent substances. The yields with coarse material are in all cases higher than these.

Microphotographs of crushed shale, purified spore case material, and spore case free residue are included to show the general form of these substances.

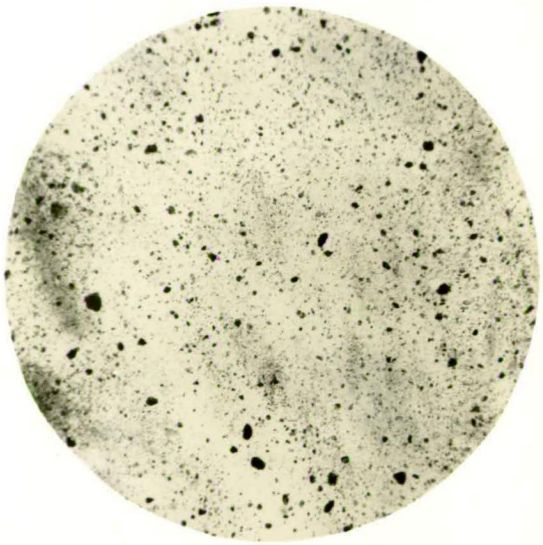
SPORE CASES x 40



SPORE CASES x 11



PULVERISED SHALE x 11



SPORECASE-FREE RESIDUE x 11

Composition of the Spore Case Material.

Spore cases were isolated from three different samples of shale in a sufficient state of purity for ultimate analysis.

These samples were

1. Soft Shale from the Tasmanite Shale Oil Co.'s mine.

2. Standard sample from the Tasmanite Shale Oil Co.'s mine.

3. The sample used in Run 34, which gave an unusually low sulphur oil and no hydrogen sulphide on distillation. This sample was obtained from the Australian Shale Oil Corporation in its time.

In general the spore cases from the first two samples were apparently very much the same, except that those from sample 1. enclosed a little less ash if anything. The spore cases from sample 3 were dark brown in colour as if they had been heated and it is possible, but not certain, that the sample had been baked by one of the frequently occurring igneous intrusions.

As regards the experimental side, the combustion tube for the carbon and hydrogen determinations was packed with sintered lead chromate but very close duplication of carbon results was not obtained for the first six or so combustions. However, after elimination of some minor troubles, satisfaction was obtained. The lead chromate did not give a quantitative absorption of the sulphur oxides present, but by running blank combustions on sugar and sulphur and on sugar and pyrites very consistent results were obtained, although somewhat high for hydrogen and a fraction of one per cent. high for carbon. It is thought that a much longer packing of chromate, or possibly a filter to absorb sulphur trioxide fumes, was needed, but, as a number of combustions had been carried out and the blank determinations checked closer than 1 milligram in the cases of both water collected and carbon dioxide absorbed, the blank correction was applied to the best determinations. It amounted to less that one-tenth per cent. in the case of the hydrogen and to approximately 0.5% in the case of the carbon.

The sulphur content of the spore cases was determined by the sodium peroxide bomb method and may be taken as correct at least to 0.02% and very probably even closer than this. The sulphur contents of the spore cases from samples 1 and 2 were exactly the same on an ashless basis.

The nitrogen content was determined by the Dumas method, using .5 gram sample. The small amount of nitrogen produced made any errors relatively great in proportion and, using 1 gram of sugar for a blank determination, it was found that .5 cc of nitrogen was obtained. This was thought to be mainly held in the pores of the copper oxide packing and only slowly given up during the course of the determination. On the amount of spore case sample taken, the correction amounted to .13% and was deducted in all cases from the gross nitrogen.

It was felt that the nitrogen figures by the Dumas method were still possibly high and, though the combustions were carried out very carefully, the amount of sample used, 0.5 gram, made small errors large in proportion. The lowest results obtained by the Dumas method were on an ashless basis

No. 1. Soft shale spore cases	0.73 % Nitrogen
No. 2. Standard sample spore cases	0.84 % "
No. 3 sample spore cases	0.87 % "

It was difficult to understand the difference between the nitrogen content of the spore cases from No. 1 and No. 2, except on the ground of experimental error, e.g., traces of carbon monoxide escaping oxidation.

Wet combustion by the Kjeldahl-Gunning method gave more consistent but also lower results all round. With all three samples the results, obtained by myself and also independently by two students, fell between 0.60% and 0.64% nitrogen. A slight difficulty in picking the end point in the titration seemed to be responsible for this variation - possibly caused by traces of certain ammines being present in the distillate.

It seems that the higher value, 0.64%, is the correct nitrogen content of the spore case material. The higher results given by the Dumas method are probably high, although the combustions were carried out very slowly and there was no carbon monoxide in the nitrogen when tested with cuprous chloride reagent. Without further work, it is impossible to say whether there is some nitrogen present in the spore case material not convertible to ammonia on moist combustion. The point is not of prime importance and the nitrogen content of the spore cases may be taken as 0.64%.

As regards the carbon hydrogen determinations, within certain limits some uncertainty exists, as analyses performed at different periods of time showed slight differences.

The last 8 analyses made deserve the most weight and the following are the results on an ashless basis:-

Analysis No.	Sample.	H	C.
3	No.2	10.20	78.3
7	No.3	10.33	82.1
8	No.1	10.18	77.5
9	No.1	10.34	78.1
10	No.3	10.56	83.05
11	No.1	10.46	79.15
12	No.2	10.47	78.45
13	No.1 another sample	10.25	78.5
14	No.2	10.21	78.5

During No. 8 analysis trouble was experienced with a loosening stopper and from No. 9 onwards another stopper was used to close the end of the combustion tube and also a new calcium chloride tube was used. This substitution had the effect of raising the hydrogen results for all samples. The calcium chloride tube used for the first 8 analyses was a somewhat poor fit into the stopper and it was thought that the higher results were correct. Analyses 13 and 14 were made with an extra long combustion tube with 50% more length of chromate packing and the hydrogen results were very much alike but lower than previously obtained.

It is obvious that the spore cases from samples 1 and 2 are very much alike in composition and can be considered to be identical within the limits of experimental error.

It is certain that the carbon percentage is very closely 78.5 in the case of samples 1 and 2 and 83.05 in the case of sample 3.

As regards hydrogen, it is within limits somewhat doubtful but, by averaging analyses 9, 11, 12, 13 and 14, 10.35% is obtained, and this is certainly within 0.1% of the correct value. Sample No. 3 may be accepted as 10.56% H.

Collecting results and taking samples 1 and 2 as identical, as they appear to be in nitrogen and sulphur also, we have

	Normal spore cases, Samples 1 & 2.	Spore cases from sample 3.
C	78.50 %	83.05
H	10.35	10.56
N	0.64	0.64
S	4.70	1.38
Oxygen by difference	5.81	4.37

On an atomic basis these are

	Normal Spore Cases	Sample 3
C	6.54	6.92
H	10.27	10.48
O	.363	.273
N	.046	.046
S	.147	.043

On the basis of C_{100} the empirical formulae are

Normal spore cases	C_{100}	H_{157}	$O_{5.55}$	$N_{.70}$	$S_{2.25}$
No. 3 " "	C_{100}	H_{151}	$O_{3.95}$	$N_{.66}$	$S_{.62}$

The nitrogen content may indicate that there is several per cent. of some protein present in the spore cases. If, on the other hand, the spore case material is homogeneous, its composition is expressed approximately by the formula $C_{143}\ H_{225}\ O_8\ N_1\ S_3$.

In the Swiss work referred to, the composition of the Tasmanite spore cases is given as $C_{90}\ H_{136}\ O_{17}$, corresponding to 72.5% carbon, 9.2% hydrogen and 18.3% oxygen. The large amount of oxygen seems to indicate that sulphur and nitrogen are included in it, but the oxygen still seems too high. The carbon-hydrogen ratio is 100 : 151, which is the same as the abnormal spore cases (sample 3). In Dana's Mineralogy, with the date 1862-4, an analysis of Tasmanite spore cases is given with apparently the nitrogen included in the oxygen as follows, carbon 79.34%, hydrogen 10.41%, oxygen 4.93%, sulphur 5.32%, corresponding to the formula $C_{100}\ H_{156.5}\ O_{4.7}\ S_{2.52}$. It appears that this analysis, with the exception of the nitrogen, is much nearer the truth than the more modern one referred to.

It will be noted on comparing the formulae that the spore cases from sample 3 and 6 hydrogen atoms short of the normal formula and approximately 3 oxygen plus sulphur atoms also. It would appear that, considering the dark brown appearance of the spore cases from No. 3 sample, they have been subject to heat in such a way as to expel hydrogen, oxygen, and sulphur in the form H_2O and H_2S. In all other samples examined no similar brown spore cases were found and it is thus concluded that these are an abnormal type and most probably have been produced by the heat treatment under certain conditions of the light brownish-yellow variety, which are therefore to be regarded as normal.

In the Swiss article the sulphur in certain spore cases occurring in the Moscow brown coal of similar age (permo-carboniferous) is stated to have been absorbed by a process similar to vulcanisation. Although only two samples have been carefully analysed, all other indications are that the normal spore cases are uniformly high in sulphur content. Within experimental error, spore cases from samples 1 and 2 were alike in carbon, hydrogen, nitrogen and sulphur content. This would indicate that, if the spore case material is a mixture of substances (resins, proteins, etc.), it is a comparatively constant mixture,

In this connection, amber approximates to the composition $C_{10}\ H_{16}\ O$ and the carbon hydrogen ratio of the Tasmanite spore cases is very similar. The spore cases are, however, definitely lower in oxygen, but contain sulphur and nitrogen in sppreciable molecular proportions.

The organic material in Tasmanite, consisting largely of spore cases, is converted on destructive distillation with ample steam into oil of

composition not greatly different from the spore cases from sample 3.

	Spore cases.	Spore cases, sample 3.	Steam distilled oil.
C	78.50	83.05	81.90
H	10.35	10.56	10.70
O	5.81	4.37	4.63
N	0.64	0.64	.27
S	4.70	1.38	2.50

It will be noted that compared with normal spore case material there has not been much elimination of oxygen but about half of the sulphur and nitrogen has been eliminated in the destructive distillation.

The small decrease in the oxygen content is partly explained by the high oxygen content of the non-spore organic material in the shale.

Composition of the remaining organic material in the shale.

This second type of organic material was not separated, on account of pressure of time, though hydrofluoric acid would probably have been effective. There is, however, no certainty that it would be anything like as inert to drastic treatment as the spore case material.

It is possible, however, by calculation to form a good idea of the composition of this material, with the aid of an ultimate analysis of the residue from the carbon tetrachloride separation. A difficulty which arises is that the amount of organic matter in, say, a gram of the spore free residue is not very certain. That is to say, the apparent ash content varies according to the method, as follows:

Open dish ignition in electric muffle 1 gm.	87.2%
Residue from combustion for carbon & hydrogen	88.08%
Calculated from proximate analysis of retort residue	85.5 %
Ash as obtained in proximate analysis of 1 gm.	86.0 %

In the proximate analysis sulphates are reduced to sulphides and the sulphur roasted off when igniting off the fixed carbon, whereas under oxidising conditions sulphate is formed from the sulphide and that which was originally present is preserved.

The higher ash thus would be the more correct to take. The lower the ash, the greater the organic matter and, since oxygen is obtained by difference, a low ash would increase the apparent oxygen content of the material. It is thus safest to take the highest ash - that from the actual combustion itself - and thus remove any doubts that the oxygen has been made to appear large. The oxygen found in this way will then be a minimum.

The data available are

Amount of residue for combustion	1.0000 gram
Ash remaining	.8808
Organic matter	.1192
Carbon found	.0789
Hydrogen found	.01217
Nitrogen in 1 gram of residue (6 gm.assay)	.00155
Sulphur content of organic matter calculated	2.0%

The ultimate composition is therefore

C	66.1 %
H	10.2
N	1.3
S	2.0
O by difference	20.4
	100.0

It will be seen that this type of organic matter is highly oxygenated. This oxygen is largely expelled as water. In Run 57, 672 grams of residue containing 80 grams organic material produced 15.5 m.l. of liquid water in addition to any vapour escaping. The liquid water corresponds to 19.4% of the organic matter.

The distillation index for this material taking this maximum ash works out at 1.14, while on the lowest ash it is approximately 1.00.

It will be noted that this second type of organic material contains less sulphur and more nitrogen than the spore case material and yields therefore an oil lower in sulphur, though not so very much lower as there is no elimination of sulphur as hydrogen sulphide on distillation.

The nitrogen content of oil 57 was found to be 0.73%, which is in accord with the more nitrogenous character of this particular type of kerogen.

PART VI.

TASMANITE SHALE OIL.

The work carried out on the oils produced from Tasmanite oil shale may conveniently be reported under two separate headings.

1. Laboratory distilled oils.
2. Commercially produced oils.

Laboratory Distilled Oils.

The general characteristics of the oils produced under laboratory conditions may be considered under the following sub-headings.

1. Distillation analyses of laboratory crude oils.
2. Specific gravity of laboratory crudes and distillates.
3. Sulphur content of laboratory crudes and distillates.
4. Nitrogen and oxygen content of crude oils.
5. Saturation of crude oils and distillates.

1. Distillation analysis of crude oils.

Over fifty samples of crude oil were produced and the majority of these were subjected to distillation analysis. It should be borne in mind that these laboratory crudes contained practically all the scrubber spirit which would be obtained in ordinary commercial working using oil scrubbers for removal of spirit from the retort gas. The efficient condensing apparatus used enabled the gas to be practically stripped of spirit before entering the oil scrubbers, so that these laboratory crudes are probably equal to a commercial crude plus scrubber spirit.

The oil scrubber catch was not separated and added to the crude, but the crude oil distilled is simply that collected in the two receivers. As regards the method of performing the distillations, the method was parallel to but not quite the same as the standard A.S.T.M. method on the same quantity, viz, 100 m.l.

A long vertical air cooled condenser was used as there was comparatively little distillate below 100°C in most cases. A 200 m.l. distilling flask was used to allow room for the frothing which sometimes occurs. The thermometer position was the standard one.

Results could be duplicated quite closely with the apparatus used, but with such a small quantity of oil the thermometric lag is relatively large in proportion to the oil quantity and this makes the first fraction larger than it would otherwise be and larger than when the distillation is carried out in a larger flask, say a 1 litre charge. In my experience, the 100 m.l. distillation gives with most of the oils examined, i.e. containing about 10% distilling below 150°C., a first fraction 2% of the original greater than a larger distillation (800 m.l.). For this reason, the distillation analyses shown in the tabulated distillation results in Part III are to be accepted with this qualification. They are, however, comparable.

In general, it may be accepted that the distillation analysis of the oil is most affected by the amount of vapour phase cracking that takes place in the retort. The oil produced in Run 14 may be taken as an example of oil in which case there has been a minimum of vapour phase cracking, while the oil from Run 33 represents the other extreme, i.e., an oil subjected to much vapour phase cracking, but not so severe as to destroy the essential nature of the oil, as happened in Runs 30 and 31. The distillation analyses for Runs 14 and 33 are

	Run 14.	Run 33	Run 26.
Sp. Gravity	0.952	0.892	0.897
- 150°C.	11.1 %	23.6 %	14.7 %
150 - 200°C.	7.8	14.0	13.9
200 - 250°C.	9.7	10.7	11.7
250 - 300°C.	11.4	18.5	15.6
Residuum	60.0	33.2	44.1
	100.0	100.0	100.0

In general laboratory distilled crudes approximate much more closely to oil 14 than to oil 33, though by slow distillation an oil more or less midway in composition is produced, e.g. oil 26.

2. Specific gravity of laboratory crude oils and distillates.

The specific gravity of Tasmanite shale oil depends partly on the sample of shale from which it is produced. Those samples which contain little spore case material produce a somewhat lower gravity oil than samples richer in this material, e.g. the oil from Run 57 was 0.911 sp. gr., while from Run 54 it was 0.921. In general, the poorer shales are poor in spore cases and produce relatively low gravity oils. This is shown in the following table.

Description	Run No.	Yield Galls./ton	Sp.Gr. of Crude Oil.
M. Band	36	2.7	0.911
"	35	6.4	0.909
"	46	7.5	0.910
"	45	9.6	0.908

In the richer shales there is much variation in the specific gravity of the crude oil produced. It seems that the standard sample produces (under laboratory conditions) an oil of rather high specific gravity, i.e. exceeding 0.920 in most cases, whereas the average of about 20 samples of shale from both top and bottom seams indicates about 0.913 as the average specific gravity of a laboratory crude.

The amount of vapour phase cracking that has taken place has by far the greatest influence on the specific gravity, as borne out by the following specific gravities of oils from the standard sample of shale:

Run	Description.	Sp. Gravity of Oil.
14	Distilled with excess steam	0.952
29	" under maximum production conditions	0.926
19	" slowly (5 hrs. oil production)	0.903
33	" with external vapour phase cracking	0.892
30	" with excessive vapour phase cracking	0.969

The effect of vapour phase cracking is to lower the specific gravity from 0.952 to 0.892, but very severe and destructive vapour phase cracking raises the specific gravity again to a new high level. This latter oil is more like a coal tar and is not strictly a shale oil as the term is ordinarily used.

During the distillation of a stationary charge of shale there is a progressive rise in the gravity of the oil produced, as seen by reference to the result sheet for Run 20, in which the oil was collected in three roughly equal separate quantities.

This distillation was carried out slowly to reduce the temperature gradient in the retort. The specific gravities are as follows:-

	Sp. Gr.	Sulphur %.
1st. portion 74 m.l.	0.896	3.18
2nd. do. 82 m.l.	0.905	2.20
3rd. do. 93 m.l.	0.922	1.70
Calculated average	0.909	2.29

Shale oils are relatively high in gravity compared with well oils and this is borne out by consideration of the gravities of the composite crude fractions distilled off in the course of the distillation analyses, as shown in the following table:-

Fraction.	% of whole.	Sp. Gr.	Saturation %.	Sulphur content.
Up to 150° C.	12.0	.767	56	2.16 %
150° - 200° C.	9.8	.832	46	2.95
200° - 250° C.	10.5	.876	38	2.83
250° - 300° C.	12.6	.912	28	2.63
Residuum	55.1	.973	10 approx.	2.10

3. Sulphur content of laboratory crudes and distillates.

Tasmanite shale oils as produced in the laboratory are fairly constant in sulphur content. Strictly, the oils should be compared with the hydrogen sulphide removed, as this compound contributes more than 10% of the sulphur content in some cases and is a very variable factor.

It has been seen that the spore case material gives much hydrogen sulphide in distillation, while the remaining organic matter contributes none, so that some of the poor shales give only a small amount of hydrogen sulphide and the oil then is free from this compound and appears somewhat lower in total sulphur. Rich shales usually give much more hydrogen sulphide and the retort gas being rich in this compound saturates the oil to a greater degree.

With the exception of the abnormal sample of shale used in Run 34, which gave an oil of 0.65% S, and the spore free residue in Run 57, which gave an oil of 1.85% S, all other laboratory crudes varied between 2.12% S and 2.61%. These figures include the sulphur as hydrogen sulphide. Although not closely investigated, it is considered that nearly all of these laboratory distilled oils, if free from hydrogen sulphide, would fall between the limits 2.1 - 2.2 % S. Even taking the total sulphur figure, it is seen that the crude oils are comparatively constant in sulphur content.

Severe vapour phase cracking will raise the sulphur content of the oil by destruction of the non-sulphurous hydrocarbons, e.g., the oils produced in Runs 30 and 31 which ran 3.20% S - 2.96% S respectively. A sample of commercially produced oil which had been severely cracked also ran over 3% sulphur.

It may be accepted that 2.5% sulphur represents the upper limit for Tasmanite shale oil produced under proper retorting conditions.

The first drippings of oil from a stationary charge at 350°C. are relatively high in sulphur, 3.15% and 61% saturated. It is possible and probable that the sulphur content further increases to a maximum and then steadily falls as distillation proceeds. This point has been partially checked in Run 20, as shown in the last table in the preceding section. The first portion of oil, approximately 30% of the whole, averaged 3.18% S, the second portion, 33% of the whole, averaged 2.20% S, and the remaining last portion, or 37%, averaged 1.70% S. The calculated average, taking into account the specific gravities, works out to 2.29%. The accompanying graph, p 268 probably closely represents the sulphur content of the distillate as the distillation proceeds.

The alteration in the sulphur content of the various fractions, previously referred to in the section dealing with specific gravity, is interesting. Repeating the table for the sake of clearness

Fraction	% of the whole.	Sp. Gr.	Saturation %.	Sulphur %.
Up to 150° C.	12.0	.767	56	2.16
150°C - 200°C.	9.8	.832	46	2.95
200°C. - 250°C.	10.5	.876	38	2.83
250°C. - 300°C.	12.6	.912	28	2.63
Residuum	55.1	.973	10	2.10

It will be seen that in these fractions, which are composite ones from Runs 10 to 19 inclusive, the sulphur content definitely increases with the boiling point to a maximum and then decreases to below the average. The higher boiling fractions are free from hydrogen sulphide but the maximum on the curve is principally due to the presence in notable amounts of thiophene homologues.

4. Nitrogen and oxygen content of crude oils.

Very little work was carried out on this phase of the investigation and only three oils were submitted to ultimate analysis, while the nitrogen content of another commercially produced oil was determined.

The oils chosen were the extremes that would be obtained in retorting. The first analysis is that of the oil obtained in determining the maximum ammonia yield of the shale and represents an oil that has

received a minimum of vapour phase cracking.

The second analysis is that of the oil obtained in Run 53 in which vapour phase cracking has been active, as the distillation was very prolonged.. Most Tasmanite shale oils would fall between these extremes, the majority of laboratory oils being nearer to the first analysis while the majority of commercially produced oils would be nearer the second analysis.

The third analysis is that of a commercially produced oil from the Tasmanite Shale Oil Co. when using the Long retort. This oil had been subjected to excessive vapour phase cracking and hardly represents average commercial oil.

The fourth analysis given is partly conjecture, as the hydrogen and carbon figures are estimated from the other analyses, particularly 1 and 2. At the same time, their total is not likely to be more than .2 or .3% in error. The nitrogen in this sample is somewhat higher than the others, but the original shale came from a different part of the field from the other shale samples. The oil was produced from shale from the Goliath Portland Cement Co.'s mine in the Crozier retort and represents a commercial oil more nearly than analysis 3.

The analyses are as follows:-

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Sp.Gr.
1. Steam distilled oil	81.9	10.7	.27	2.50	4.6	.952
2. Very slow distillation R 53	83.7	11.05	.28	2.37	2.6	.898
3. Commercial oil T.S.O.Co.	83.4	10.90	.34	3.35	2.0	.912
4. Commercial oil Crozier retort	82.5?	10.8?	.53	2.48	3.7?	.940
5. Oil from spore free residue R 57	n.d.	n.d.	.73	1.85		.911
Spore case material	78.5	10.35	.64	4.70	5.8	

By comparing the analysis of steam distilled oil with that of spore case material, it will be seen that there has been an elimination of approximately half of the sulphur and of the nitrogen, whereas the oxygen has not been greatly reduced. The carbon and hydrogen percentages rise in accord with the reduction in the other three elements.

A steam distilled oil is therefore not only highly unsaturated but highly oxygenated and would give higher refining losses than would be obtained with an oil which had been subjected to vapour phase cracking in the retort or otherwise. The oxygen content of oil 53 is nearly reduced to half that of the steam distilled oil, but the nitrogen content is little changed. The first three analyses are of oils derived from shale from the Tasmanite Shale Oil Co.'s leases, while No.4, in which the nitrogen is higher, is from a different portion of the field.

It would seem that the nitrogen content of the oil is influenced more by the type of shale than by the treatment of the shale in distillation. Not very much attention has been paid to the nitrogen content of the oil, as it is relatively easily removed, since the nitrogenous compounds are basic and dissolve readily in the refining acid. At the same time, it is true that they contribute much to the unpleasant smell of the crude oil, but again washing with quite dilute acid will extract the basic compounds. Vapour phase cracking appears to have comparatively little influence on the nitrogen and sulphur contents of the oils, but the oxygen content is much reduced by this treatment. It has been well said that refining begins at the retort, and this applies with most force to the oxygen content of the oil.

5. Saturation of Crude Oils and Distillates.

The "saturation", or percentage of oil insoluble in excess of concentrated sulphuric acid, has been determined on a number of distillates, as well as on all the crude oils made. The determination is difficult and inconclusive on highly unsaturated and comparatively viscous crude oils, unless suitable precautions are taken. The method of making the determination which was found satisfactory and sufficiently accurate was to measure out from a specially made pipette 2.5 m.l. of oil into a centrifuge tube made from a burette and accurately graduated. 7.5 m.l. of sulphuric acid of 1.84 sp. gr. were then added and the whole thoroughly mixed and allowed to stand ten minutes. The resultant heat development afforded a very fair preliminary idea of the amount of unsaturates present. After reaction, centrifuging was carried out till the oil layer resting on the dark acid layer was constant in volume. One or two minutes was sufficient for most oils, but oils with 85-90% unsaturates required ten minutes at least.

The results are probably in most cases accurate to 1 to 2%, but the difficulty of ascertaining the upper oil surface precludes a more accurate determination. Settlement methods were found to give unreliable and erratic results.

The saturation of the 50 crude oils produced in the laboratory are given in the tabulated results of distillations in Part III.

It will be seen that the saturation varies from 14% in the case of distillation with excess steam, as in Run 14, to 44% for Run 53, which was the slowest distillation made on the same shale (Standard sample). These figures indicate the differences in the nature of the oil produced from the same sample of shale by varying distillation conditions. For ordinary simple distillation on the same sample, the

saturation figures averaged about 25 - 30%, while for a laboratory distillation carried out at the same rate as a commercial distillation, e.g. Run 19, the saturation of the oil was 36%.

On other samples of shale, e.g. Runs 35 to 48 inclusive, 51, 56 and 58, or 17 samples in all from both mines, the saturation of the crude oil averaged 30-35% when distilled at rates of heating of about 100°C. per hour. Slower distillation would give higher saturation figures.

In Run 34 on an abnormal shale, the oil ran 50% saturation, but this is distinctly unusual.

During the course of a distillation with a stationary charge, the saturation gradually decreases. The first runnings of oil proved to be 61% saturated and this progressively drops as distillation proceeds.

For the same sample of shale the saturation of the crude oil is very approximately indicated by the specific gravity - oils of .900 gravity or slightly less are approximately 40% saturated, while oils of .950 gravity are approximately 15%. This corresponds to about 1% increase in saturation for each increase of .002 in the gravity of the crude oil.

As regards the saturation of crude distillates, the following table also given earlier gives a close idea of the saturation of the average fraction of laboratory oil:-

Fraction	% of whole	Sp. Gr.	Saturation %	Sulphur %.
up to 150°C.	12.0	.767	56	2.16
150°C.-200°C.	9.8	.832	46	2.95
200°C.-250°C.	10.5	.876	38	2.83
250°C.-300°C.	12.6	.912	28	2.63
Residuum	55.1	.973	10 approx.	2.10

It will be seen that the lowest boiling fraction is only 56% saturated and that the saturation decreases with increase of boiling point.

In the corresponding fractions from commercial crude Tasmanite shale oil, a higher saturation would be shown, owing to the greater vapour phase cracking in the retort, but the difference is not large.

It will be appreciated that a crude petrol only 60% saturated presents unusual refining difficulties, owing to the potential solubility of over 40% of the petrol in sulphuric acid.

The percentage saturation of an oil is easily determined, but it is nevertheless a somewhat ambiguous term. The unsaturates as measured by solubility in sulphuric acid include the unsaturated hydrocarbons of various series, the basic heterocyclic compounds, and practically all of the aromatics if the acid is sufficiently concentrated and sufficient excess is used. The partition of the oxygenated acid oils between the acid layer and the paraffinic layer is uncertain in the case of Tasmanite oil. However, the paraffins and cycloparaffins are insoluble in the acid and the saturation is an approximate measure of these. On crude distillates containing the acidic and basic oils, as well as unsaturated hydrocarbons, aromatics, thiophenes, naphthenes and paraffins, the percentage of saturation, determined by mixing with three volumes of 1.84 sp. gr. sulphuric acid and centrifuging after reaction, is higher than obtained by successive extraction with excess of sodium hydroxide solution, excess of 10% sulphuric acid, 2 volumes of 80% sulphuric acid and 2 volumes of 98% sulphuric acid. The extra handling may account for part of the discrepancy, but the total of the paraffins, naphthenes, and acidic oils together falls 3%-5% below the saturation percentage determined in the usual way. This discrepancy of 3-5% is not explainable by handling losses, as much care was used to avoid evaporation and wet surface losses. The greater total volume of reagents used may account for part by solution. In any case, the saturation figure is within several per cent. an index of the paraffin and naphthene content and for commercial work is of sufficient accuracy for many purposes.

Later work has shown that the proportion of aromatics and thiophene homologues, as measured by the loss of oil by solution in 2 or 3 volumes of 98% sulphuric acid following on treatment by 83% acid to previously remove unsaturates, is large. There is a decided difference in the apparent percentage of aromatics if 95% acid is used for their removal instead of 97.5 to 98.0% acid, and for their complete removal acid of 98% strength is necessary. In the saturation test, using 3 volumes of even 98% acid, there is such a large proportion of unsaturateds, basics, and aromatics present that the resultant acid strength at the final equilibrium point is probably too low to sulphonate all the aromatic class, so that the insoluble oil is not all paraffins and naphthenes. If acid of 1.84 sp. gr. as usually specified is used - and this may only be 95% or little over - then the saturation percentage, using three volumes of acid is decidedly higher than the paraffin and naphthene content - as much as 10% of the original oil volume in the case of certain Tasmanite shale oil distillates.

The saturation figures given in Part III and elsewhere must therefore be taken as largely comparative and with a certain amount of reserve, as indicating the paraffinic and naphthenic content of the oil, and in general they show the oil in a more favourable light from a refiner's point of view than is actually the case.

Commercially Produced Tasmanite Shale Oils.

Much work on a Commercial and semi-commercial scale has been carried out by Mineral Oils Extraction Ltd. and, on this account, comparatively little work was done in this laboratory on the oil produced by the Crozier retort. These Crozier retort oils resembled more closely the laboratory produced oils than do the oils produced by the Tasmanite Shale Oil Co. in the Long retort in 1930 and upon which most of the following work described was done.

Before proceeding to discuss the work on the T. S. O. Co.'s oil, a few available figures on oil from the Crozier retort are of interest.

In July 1930, three samples of crude oil were obtained. These were from different points in the condensing system and were called light crude, heavy crude, and crude oil. Some values of specific gravity, saturation and sulphur content are given below.

Crozier Oils.

	Sp. Gr.	Saturation %	Sulphur %	Nitrogen %
Light crude oil	0.885	N.D.	3.01	N.D.
Heavy crude oil	0.940	31	2.48	0.53
Crude oil		N.D.	2.44	N.D.

The latter sample was passed on for determination of the calorific value after the sulphur content was determined and nothing further was done. It was, however, practically the same as the heavy crude in viscosity and probably the other constants also. These figures are very meagre, but sufficient to indicate that in sulphur content and saturation they are fairly similar to laboratory distilled oils.

The general high sulphur content of Tasmanite Shale Oil was further shown by two samples of oil produced by the Pumpherston retort erected and operated by the Shale Oil Demonstrating Company on the site of the Australian Shale Corporation Works. The abnormal sample distilled in Run 34 came from this property, and its low sulphur content was quite unusual for the Latrobe field. The examination of the two samples of oil was therefore undertaken with a good deal of interest. The results showed very definitely that the oil was of the same general character and high in sulphur, and also that it was deficient in the heavy fractions which were apparently accumulating in some part of the condensing system.

The results are

Pumpherston Oil.

Date.	Sp. Gr.	Saturation %.	Sulphur %.
June 4th.,1932	.878	54%	3.05
June 25th., 1932	.913	48%	2.79

The low gravity and relatively high saturation and sulphur content of both oils, together with the change in all these figures over several weeks, clearly indicate that either distillation was not complete or,more probably, that the large condensing system (compared with the one retort) was trapping some of the heavier part of the oil.

It is quite clear that the oil from shale on the Australian Shale Corporation's side of the Mersey river is of the same order of sulphur content as the other oils examined and in its other characters shows no essential differences.

Tasmanite Shale Oil Company's crude oil.

This oil, which was the subject of much work, was produced in the Long retort towards the end of its life in 1930. One four gallon tin was obtained in April 1930, and, as this was from storage tanks and appeared to be deficient in the lower boiling fractions, another four gallons of crude oil direct from the condenser was obtained in May 1930. It was not greatly different from the first sample and both were used. The distillation analyses were as follows:-

	100 m.l.		800 m.l.	
	1st. Sample.	2nd. Sample.	1st. Sample.	2nd. Sample.
Up to 150°C.	4.7		2.0	4.4
150°C. - 200°C.	14.0		13.6	14.4
200°C. - 250°C.	13.3		16.3	15.6
250°C. - 275°C.	9.3		8.1	9.4
Residuum & loss	58.7		60.0	56.2

	1st. Sample	2nd. Sample.
Specific Gravity	0.929	0.912
Saturation	36 %	40 %
Sulphur content	3.34 %	3.35 %
Nitrogen content	N.D.	.34 %

With these oils there is very little distillate below 130°C., indicating that the lower boiling oils had not been recovered.

The ultimate analysis of the 2nd. sample is as follows:-

Carbon 83.4%, hydrogen 10.9%, nitrogen .34%,
Sulphur 3.35% oxygen 2.0 %

Approximately 6 litres of the first sample were distilled and separated into two fractions - a combined motor fuel fraction cut at 275°C. and residuum. About 40% of the crude motor fuel fraction was obtained and this was redistilled and a small residue of .941 sp. gr. added to the residuum.

Results 1st. distillation

Up to 275°C.	39.7 %	sp. gr.	.866	Saturation 50%
Residuum	60.3 %		.968	
After redistillation of 1st. fraction				
Up to 275°C.	36.3 %	Sp. Gr.	.859	
Residuum	63.7 %	"	.970	

The portion over at 275°C. was refined by the hypochlorite method as given in a subsequent section.

Larger scale distillations were made with an oil drum for a still and 11 litres of the 1st. sample of oil distilled. A 12 bulb fractionating colums was used. The percentages over at different temperatures were as follows:-

Fraction.	%
Up to 100° C.	0.5
100°C. - 150°C.	2.5
150°C. - 185°C.	9.4
185°C. - 227°C.	12.7
227°C. - 290°C.	18.5
Residuum by difference	56.4

The distillates were combined into 3 fractions up to 185°C., 185-227°C., 227-290°C. and soda washed for removal of hydrogen sulphide, creosote etc., and then washed with 10% sulphuric acid for removal of basics.

The following are the losses incurred in these treatments:-

	Loss by NaOH Washing.	Loss by H_2SO_4 washing.
- 185°C. fraction	5.9 %	1.5 %
185°C. - 227°C. "	6.4 %	2.9 %
227°C. - 290°C. "	7.4 %	3.0 %

The second sample of oil was distilled in a 16 litre batch with the 12 bulb fractionating column and with the thermometer at the vapour off-take. More water was present in this sample, which was not such a

thoroughly settled oil as the 1st. sample. This may account for the greater volume of the fractions compared with the 800 m.l. distillation, but it is thought that cracking was also taking place.

The following are the volumes of the fractions at the different temperatures:-

Temperature.	Volume of Fraction.	% of whole.
0 - 100°C.	.13 litres	0.81%
100 - 125°C.	.17	1.06
125 - 150°C.	1.00	6.25
150 - 175°C.	1.10	6.87
175 - 200°C.	1.07	6.69
200 - 225°C.	1.11	6.94
225 - 250°C.	0.63 ?	3.94 ? 6.30 probably
250 - 277°C.	1.35	8.44 ? 6.08 "
Residuum by difference and loss		59.0

It will be seen from the table given above that the amount of distillate for each 25° increment is approximately constant, once real boiling has commenced about 120°C. The 225-250°C. fraction and the 250°C-277°C. fraction seem anomalous from the recorded figures. It would seem that the 240°C. mark on the thermometer was mistaken for the 250°C. mark. On this assumption and multiplying the volume of the 225-250°C. fraction by 25/15 the figure 6.3% is obtained, which appears correct. The 250-277°C. fraction then reduces to 6.08%, which also appears to be very probable.

This oil is thus seen to be deficient in the lower boiling oils and different from the laboratory crudes, which usually boil freely about 70°-80°C. The deficiency of low boiling fractions was due to poor condensation of the light oils. It is also probable that a large volume of gas was being made and that dilution of the retort gas with air was occurring. Both of these factors would tend to prevent proper recovery of light oils. As a representative Tasmanite shale oil, it has to be taken with reserve. Its general characteristics, such as high sulphur and low oxygen content and deficiency of low boiling oils indicate that it is an oil which has been subjected to much cracking in the retort and is devoid of the lower boiling hydrocarbons etc. usually present in Tasmanite shale oil. However, it is a type of oil which may easily be produced in commercial operating, and it is not so very different from an average commercial oil as to lessen the value of the results.

The crude distillates were combined into 3 samples - 175°C., 175-225°C., and 225-277°C., each about 2 litres volume, for further treatment.

The following table shows the figures obtained during the purification of these fractions with 10% caustic soda and 10% sulphuric acid.

	Fraction. 120°C.-175°C.	175°C.-225°C.	225°C.-277°C.
Specific Gravity	.799	.849	.899
Saturation %	64	57	48
Sulphur content crude	3.47 %	3.18 % ?	3.14 %
Percentage of original fraction lost by washing with soda till volume was constant	2.90 %	5.04 %	6.67 %
Sulphur content now	3.16 %	3.38 %	3.08%
Percentage of original fraction lost by washing with 10% acid till volume was constant	1.38 %	2.52 %	4.85 %
Sulphur content now	3.20 %	3.46 %	3.12 %
Saturation of oil	56 %	50 %	38 %
Specific gravity	.795	.842	.900
Total loss of oil	4.28 %	7.56 %	11.52 %

After soda washing, the oils are much improved in smell, as the hydrogen sulphide (especially in the first fraction) and creosote is removed, but the oils still have the very characteristic clinging smell which is due to the nitrogeneous compounds.

In washing the fractions from 27 litres of crude oil, 632 m.l. was removed as soluble in the caustic soda solution. On acidification of the combined caustic liquors, 330 m.l. of dark red creosote separated. This corresponds to about $1\frac{1}{4}$ % of the original crude oil distilled and represents slightly over half of the caustic refining loss.

The oils were decidedly darkened by 10% acid washing, both with hydrochloric as well as with sulphuric acid, and a subsequent caustic soda wash removes no colour. The acid washed were coloured dark brown also. The acid washed oils showed a strong purple fluorescence which disappeared on standing some time.

With dilute acid washing, as with soda washing, the refining loss increased with the boiling point and becomes quite considerable in quantity. In general alkali washing removes twice as much oil as does acid washing. This helps to explain why shale oils give such high refining losses, as here no unsaturated hydrocarbons were removed. The acid washings were made alkaline separately and the nitrogenous bases recovered. Beyond noting that they increased in volume with

the boiling point, and that the lower boiling fractions gave the most obnoxious smelling bases, no work was done on these. These bases, especially from the lower fraction were exceedingly powerful in smell and very obnoxious. Pyridine could be smelt distinctly, but other compounds were present also. These basic oils once touched on the skin remained there (by smell) after repeated washing in soap and water. Much of the characteristic clinging smell of Tasmanite shale oil is due to these basic oils. The oils purified from hydrogen sulphide etc., creosote, and basic nitrogenous oils are relatively free from smell, indicating that the sulphur compounds which are present in such quantity as to bring the sulphur content up to 3% or over, have comparatively little smell.

Popularly, sulphur is blamed for most of the smell of Tasmanite oil, but it appears much of the onus must be placed on the heterocyclic nitrogen compounds.

The creosote and basic-free fractions were at a later date treated to determine the proportions of unsaturateds and aromatics present and also to gain some idea of the proportions of paraffins and naphthenes present in the oil insoluble in 1.84 sp. gr. sulphuric acid. This work is reported in Part VII.

Application of the hypochlorite process to Tasmanite shale oil distillates.

Owing to the large unsaturated hydrocarbon content of the distillates (laboratory produced crude petrol fractions are over 40% unsaturated) refining processes involving the use of sulphuric acid must prove very wasteful, both of reagent and oil. The hypochlorite process as developed by the Anglo-Persian Oil Co. to effect desulphurisation in the presence of aromatics was naturally turned to as a possible solution of the refining problem. The main common type of sulphur compound that it is ineffective on is thiophene and its homologues.

Work on combined petrol and kerosene fraction.

The first hypochlorite purification carried out was on a combined petrol and kerosene from the first sample of T.S.O. oil, fraction distilling over below 275°C. This treatment was similar in this regard to the practice at the Commonwealth Oil Refineries.

There was very little distillate below 100°C. so that the fraction was really a 100°C.-275°C. cut of .859 sp. gr., 50% saturated, and containing 3.47% sulphur, including hydrogen sulphide.

The oil, was treated in the following manner:-

1. 500 m.l. of oil washed with an equal volume of 10% sodium hydroxide solution.

2. Again washed with 500 m.l. of 10% sodium hydroxide solution.

3. Shaken with 500 m.l. of .3 N N_aOCl solution. This solution was exhausted of its N_aOCl content.

4. Shaken with 500 m.l. of .3 N N_aOCl solution. This solution was also practically exhausted.

5. Shaken with 500 m.l. of .3 N N_aOCl Solution. This wash was reduced to .075 N N_aOCl.

6. Dilute soda wash followed by water.

7. Redistillation to 275°C. Residue only a few m.l. which were discarded.

The total refining losses were 11% of the original volume and the apparent saturation of the oil 58%.

Samples were taken for sulphur content after stage 2 and at the end, and ran as follows:-

Crude fraction	3.47% S.
Soda washed fraction	3.15% S.
Refined oil	3.10% S.

A repeat of this work using 500 m.l. of the same fraction was carried out. Two soda washed were given and ten hypochlorite washes till the oxidation was complete. Soda and water washes were then given, but redistillation omitted. No samples were taken out and the work was conducted with the utmost care. The refining loss was lower than the previous time, and was 9.0%. This is no doubt a more accurate measure of the refining loss on the fraction.

The final oil ran 3.17% sulphur.

Considering the two cases, it is seen that, after the first soda washing, the sulphur elimination by the hypochlorite treatment only keeps pace with the diminution of oil volume. Evidently the oxidised sulphur compounds are too oil soluble to be removed by water washing and/or the main bulk of the sulphur is thiophenic.

The large chlorine absorption may be accounted for by absorption of chlorine by the unsaturated hydrocarbons in spite of carefully controlled alkalinity. The chlorine content of the oil was not determined, but it is believed that much of the available chlorine that was used up remained in the oil.

The redistilled oil was quite yellow, even in fractions boiling about 150°C.

Work on petrol fraction alone.

It was thought that the presence of the kerosene fraction may have militated against the success of the process, so that further work was confined to a fraction cut at 175°C., approximating a petrol fraction.

A careful hypochlorite treatment with alkalinity controlled, as recommended by the originator of the process, was carried out on 500 m.l. of fraction that had already been alkali and dilute acid washed and contained 3.20% S. It was washed with three successive litres of .3N N_aOCl solution. These washes were 100%, 92% and 90% spent, respectively. The oxidation was rapid up to .55 N or 1.1 N on the oil, i.e., approximately 40 gms. chlorine per litre, and then slowed down. The total oxidation was equivalent to 70 grams of chlorine per litre of oil. The oil was then washed with 10% caustic soda, 1% soda, and then water.

The refining loss was 24 m.l. = 4.8%, which corresponds to 4.6% of the original crude fraction. There already had been a loss by the preliminary alkali and dilute acid washing of 4.3%, making the total loss 8.9%. This closely confirms the 9.0% loss in the previous work on the -275 fraction.

The treated oil was distilled and collected in fractions of which the sulphur content was determined. The initial boiling point of the treated oil was 100°C. and the oil darkened on heating. The fractions were soda washed after distillation to remove acid vapours and, incidentally, some yellow colour. The following results were obtained:-

Fraction	Colour.	Sp.Gr.	Volume	% S.	Grams Sulphur.
- 125°C.	pale yellow	.774	105 m.l.	2.27	1.85
125°C.- 150°C.	yellow	.794	190	2.74	4.14
150°C.- 175°C.	darker yellow	.811	118	2.59	2.49
+ 175°C.	dark brown	.854	63	2.64	1.42
					9.90

Sulphur content of treated oil computed 2.59%.

Sulphur contained in alkali and acid washed oil

500 m.l.	.800 Sp. Gr.	at 3.20% S.	=	12.80 grams.
Sulphur present in fractions				9.90 "
Eliminated from oil in treatment				2.90 "
Percentage of sulphur removed in treatment				22.6 %

A second purification was then made on this -175 fraction for checking purposes.

500 m.l. of alkali and acid washed -175 fraction were taken and washed with 3 successive litres of .3N sodium hypo chlorite solution. The first two litres were rapidly reduced in strength to .015 N, and the third litre was reduced to .075 N before the reduction became very slow.

The hypochlorite used was equal to 1 litre of .8 N or 28.4 grams active Cl. This corresponds to 57 grams chlorine per litre of oil.

The oil was then washed with 10% sodium hydroxide, followed by very dilute acid to clarify the oil. The oil volume was then 476 m.l., showing a refining loss of 4.8% or 4.6% of original crude fraction. This loss was exactly the same therefore in both purifications.

This purified oil was not assayed for sulphur, but it was separated by distillation into two portions by distilling and cutting at 200°C. The distillate was 450 m.l. of a yellow oil of acid smell. It was soda washed before running the sulphur determination. The residue was 15 m.l.

The following results were obtained:-

Fraction	Sp. Gr.	Volume	% S.	% Satn.	Grams S.
- 200	.794	450 m.l.	2.60	66	9.30
Residue	.920	15 m.l.	3.25	-	.45

Sulphur contained in acid and alkali washed oil				
500 m.l.	.800 SP.Gr.	at 3.20% S.		12.80 grams.
Sulphur present in distillate and residue				9.75 "
Eliminated from oil in treatment				3.05 "
Percentage of sulphur removed in treatment				23.8 %

The results of these two purifications on the same fraction check very closely as regards sulphur elimination, 22.6% and 23.8%. In the second case the distillation to 200°C. seemed to result in the loss of about 2% of the oil, and taking this into account the results are practically identical.

It is obvious that on fractions of this type the hypochlorite process is totally unsuitable, and accordingly no further attempt was made to investigate the hypochlorite process.

The poor elimination of sulphur indicates with great probability that the bulk of the sulphur is in heterocyclic compounds such as thiophene and its homologues.

The hypochlorite purified oil is much pleasanter in smell, as there has been an oxidation and removal of some of the sulphur compounds and the sickly smell of the unsaturates has been replaced by the clean terpene like smell of the chlorinated hydrocarbons. The chlorine content of the oil was not determined, but was undoubtedly high, as most of the active chlorine of the hypochlorite was in all probability retained by the oil.

A few sporadic attempts were made to reduce the sulphur content of the -175 fraction, as follows:-

(a) 100 m.l. of alkali and acid washed -175 fraction 3.20% S. were shaken in a large separatory funnel with 2 litres of 10% sulphuric acid and a few grams of potassium permanganate added from time to time. Total permanganate used 40 grams for 100 m.l. oil.
Refining loss 17%.
Sulphur content of treated oil 1.00%.

(b) 100 m.l. of hypochlorite purified -175 fraction of 2.60% S. were treated with thorough agitation with two lots each of 20 m.l. of 95% sulphuric acid in succession. After final settlement and soda and water wash, only 59 m.l. of oil remained, or 41% refining loss.
The sulphur content of the treated oil was .86%

(c) 20 m.l. of hypochlorite purified fraction was agitated with 200 m.l. of 10% mercuric acetate. A precipitate of waxy nature was formed, removing nearly all the yellow colour of the oil and 20% of its volume.
The sulphur content of the treated oil was 1.81%.

It will be noted from these three cases cited that the sulphur compounds are very difficult to remove from the oil and even 40% of sulphuric acid fails to remove all the sulphur compounds.

It is admitted that the acid was not used in the most efficient way, but the indications are that acid of this strength sulphonates the sulphur compounds but slowly. Work at a later date at the mineral oils extraction plant indicates that oleum is a much more efficient sulphonator and remover of these sulphur compounds, but opportunity has not presented itself to investigate this point in

this laboratory.

The following of the removal of the sulphur with 95% sulphuric acid used in small amounts is given in the following section.

Desulphurisation of petrol and kerosene fractions by 95% sulphuric acid.

Two distinct tests were carried out

1. on alkali and acid washed - 175°C. fraction.
2. on " " " " 175°C-225°C. fraction.

The general procedure was the same in each case, and the technique was designed to ascertain the effect of each successive 1% by volume of the acid.

1. Work on - 175°C. fraction.

The general operations were as follows.

500 m.l. of acid and alkali washed - 175°C. fraction were shaken for 30 minutes with 5 m.l. of 95% sulphuric acid, and settled all night.
Oil volume now 487 m.l. Sp. Gr. in acid state .796.
Took off 1/5 = 97.5 m.l. and soda washed with 100 m.l. of 25 g/litre sodium hydroxide.
Oil volume 97.0 m.l.
Rewashed part with 100 gram/litre sodium hydroxide to see if further diminution of volume occurred, result negative.
Saturation 64% ~~oil~~.
Sulphur determination made on 2nd. soda washed oil 3.15%. Acid used 1% by volume.
Took 4/5 of 487 m.l. of preceding oil before soda washing and added 4 m.l. of sulphuric acid. Shaken occasionally with standing for one hour, settled, Oil volume now 380 m.l.
Took 1/4 or 95 m.l. and washed with 100 m.l. of 2½% sodium hydroxide solution.
Volume of portion 94.5 m.l. Sp. Gr. .792. Saturation 66%.
Sulphur content 2.94%.
Total acid used 2% by volume.
Took 3/4 of 380 m.l. = 285 m.l. of preceding oil before soda washing. Shaken with 3 m.l. of sulphuric acid for 30 minutes and separated, volume now 278 m.l.
Took 1/3 = 93 m.l. - soda washed as before. Water washed but oil emulsifies on washing with water after soda wash. Lost a little oil. Volume now 90 m.l. of Sp. Gr. 1794.
Saturation 68%. Sulphur content 2.73% but result may be a

few hundredths of one per cent low.
Total acid used 3% by volume.

Took 2/3 of 278 m.l. = 185 m.l. of preceding oil before soda washing. Shaken with 2 m.l. sulphuric acid for 30 minutes and separated. Volume now 180 m.l.

Took $\frac{1}{2}$ = 90 m.l. - soda washed and water washed. Oil emulsifies considerably on water washing. Recovered oil 88.5 m.l. Sp. Gr. .795. Saturation 69%. Sulphur content 2.65%.
Total acid used 4% by volume.

Took $\frac{1}{2}$ of 180 m.l. = 90 m.l. of preceding oil before soda washing and agitated with 1 m.l. sulphuric acid for about 1 hour on account of small amount of acid. Volume of oil actually measured 85.5 m.l. Soda washed, emulsion formed and oil lost. Repeated acid treatment makes oil liable to emulsify. Volume of washed oil 80 m.l. Sp. Gr. .796. Saturation 70%. Sulphur content 2.58%.
Total acid used 5% by volume.

The colour removal without distillation was continuous up to 4% acid, but the 5% acid treatment left more colour than the 4%. The palest coloured petrol was a very pale straw and distilled sparkling water white.

In the following collected results, the volumes of oil left after acid treatment are given as measured directly after acid and before alkali washing, but the figures for gravity, saturation and sulphur content refer to the oil after alkali washing.

Collected Results on - 175°C. fraction.

Sample.	Volume.	Sp.Gr.	Saturation. %	% S.	Grams Sulphur.	Stage removal.	Total % removal.
Original.	100	.795	62	3.20	2.54	0.0	0
1% acid	97.5	.796(acid)	65?(64)	3.08	2.38	0.16	6.3
2% acid	95.0	.792	66	2.94	2.21	0.17	13.0
3% acid	93.0	.794	68	2.73+	2.02	0.19	20.5
4% acid	90.0	.795	69	2.65	1.90	0.12	25.2
5% acid	85.5? (87.5)	.796	70	2.58	1.80	0.10	29.2

A few determinations are slightly in error and more probable figures are indicated in brackets.

It will be noted that the sulphur removal is approximately proportional to the amount of acid used, averaging about 6% of the total sulphur present per 1% of acid used. The amount of oil removed by the treatment is approximately 2.5 times the acid used. Working in this way, it would take approximately 16-17% of acid to dissolve all the sulphur compounds, and with this amount of acid all the unsaturated hydrocarbons would be removed also.

The sulphur removal for 2 or 3% acid as used in Scotch refining practice leaves Tasmanite shale petrol still with the bulk of the sulphur content untouched.

Work on 175-225°C. Fraction.

Took 500 m.l. of alkali and acid washed 175-225°C. fraction of .842 Sp.Gr., 58% saturation and 3.46% Sulphur.
This was shaken with 5 m.l. of 95% sulphuric acid and settled overnight.
Volume of oil 488 m.l.
Took 1/5 = 97.5 m.l.& soda washed as before, Sp. Gr. of oil .840, 61% saturated, sulphur content 3.46%. Acid used 1% by volume.

Took 4/5 of 488 m.l. = 390 m.l. of preceding oil before soda washing and washed with 4 m.l. of acid. Separated acid tar.
Volume now 380 m.l.
Took 1/4 = 95 m.l. and soda washed as before. Sp. Gr. of oil .839, saturation 63%, sulphur content 3.38%.
Total acid used 2% by volume.

Took 3/4 of 380 m.l. = 285 m.l. of preceding oil before soda washing and washed with 3 m.l. of sulphuric acid.
Separated acid tar.
Volume now 280 m.l.
Took 1/3 = 93 m.l. and soda washed but no water wash.
Volume 92 m.l. Sp. Gr. of oil .837. Saturation 65%.
Sulphur content 3.32%.
Total acid used 3% by volume.

Took 2/3 of 280 m.l. = 186 m.l. of preceding oil before soda washing and washed with 2 m.l. sulphuric acid. Separated acid tar.
Volume now 180.5 m.l.
Took $\frac{1}{2}$ = 90 m.l. and soda washed but no water wash.
Volume 89 m.l. Sp. Gr. .835. Saturation 66%. Sulphur content 3.17%.
Total acid used 4% by volume.

Took $\frac{1}{2}$ of 180 m.l. = 90 m.l. of preceding oil before soda washing. Washed with 1 m.l. of sulphuric acid. Separated acid tar. Volume now 88 m.l. Soda washed but no water wash.
Volume now 87 m.l. Sp. Gr. .836. Saturation 68%.
Sulphur content 3.02%.
Total acid used 5% by volume.

In the following collected results, the volumes of oil given refer to that left after acid washing, as additional losses in handling occur with the soda washing. It is thought that the adoption of the oil volume after acid treatment and the figures for sulphur etc. on the alkali washed oil give the most accurate picture of the sulphur removal.

Collected Results on 175°C.- 225°C. Fraction.

Sample.	Volume.	Sp. Gr.	Saturation. %	% S.	Grams Sulphur.	Stage Removal grams.	Total % Removal.
Original	100	.842	58	3.46	2.92	0	0
1% acid	97.5	.840	61	3.46	2.84	.08	2.7
2% acid	95.0	.839	63	3.38	2.70	.14	7.5
3% acid	93.0	.837	65	3.32	2.58	.12	11.6
4% acid	90.0	.835	66	3.17	2.38	.20	18.5
5% acid	88.0	.836	68	3.02	2.22	.16	24.0

It will be noted that there is comparatively little removal of sulphur with the first 1% of acid. The sulphur determination is liable to an error of about .02%, though usually closer checks than this were obtained in duplicate assays. It is possible that the small removal with the first treatment is due to these small errors in the sulphur determinations. For the same reason, the sulphur appears a little irregular right through and this is accentuated by the difficulty of measuring small quantities of volatile oil accurately, as handling has to be expeditious and then there is always the wet vessel problem. In order to do this work more accurately, larger volumes would have to be used. However, the figures obtained all through have been given as recorded and within fairly small limits the work is accurate.

The main conclusion to be drawn is that the sulphur removal in the case of both fractions is progressive but slow, and at the rate of removal the high sulphur content of these oils is but slowly reduced. At the same time, in the case of both fractions, each acid treatment removes 2.5 times its volume of oil, partly sulphur compounds, but principally unsaturated hydrocarbons.

Sulphur removal from Tasmanite shale oil distillates by 95% sulphuric acid is slow and imperfect and the repeated treatments, or the relatively large quantity of acid necessary, remove a considerable amount of oil, resulting in much refining loss and producing large quantities of acid tar. Experiments made at the Mineral Oils Extraction Ltd. plant at Latrobe with oleum (precise strength unknown) indicated that sulphur removal was far better

with oleum. From information supplied, it appears that, working with crude petrol of about 2.5% sulphur and containing added scrubber spirit which is more saturated and therefore less attacked by the acid, sulphur can be reduced to .86% with 3% oleum, and to .37% with 5% of oleum. The loss of oil volume in oleum treatment is roughly 3% per 1% oleum used with the more saturated crude petrol used. With crude petrol as used in the work reported in this section, the losses would be undoubtedly higher, as the oleum treated petrol was more saturated to begin with. The loss of oil in both acid and oleum treatment can approximately be considered as proportional to the equivalent H_2SO_4 content of the acid or oleum.

As Mineral Oils Extraction Ltd. were working on oleum for sulphur removal, this phase of refining was not proceeded with in this laboratory, but no fine details are available of the work done at Latrobe on this point.

It would seem certain that of all the methods of sulphur removal from Tasmanite shale petrol, oleum treatment is the most effective and promising and if, from economic or other causes, the refining of shale petrol needs to be undertaken again, then a proper investigation of oleum treatment should be looked on as the starting point.

Crude petrol that has been treated with 4% of sulphuric acid after removal of basics will distil nearly white, but if it has been vapour phase cracked as in Run 33 it will distil white. The spirit is, however, not stable, but yellows and deposits gums. An additional 1% of acid makes the distilled petrol water white and much more stable, but gums are deposited in time, but with vapour phase cracked oil, as in Run 33, 2% of acid is sufficient to give on later distillation a spirit of water white colour and free from gum-forming properties. The smell, however, is still a characteristic shale one and is due to the large amount of unsaturates still present. The more protected the oil is from vapour phase cracking in the retort, the greater the difficulty of removing gum-forming constituents from the petrol. It seems probable, if refined petrol were the principal object, that the most economic working would be obtained by allowing a moderately large amount of vapour phase cracking to take place in the retort, or external to it in a special apparatus, and sacrificing about 25% of the assay oil yield. The remaining oil would then possess much higher quantities of the lighter fractions and these would be much more easily refined. The question of liquid phase cracking is an open one, but it is expected that the highly unsaturated Tasmanite shale oil would prove exceedingly troublesome in excessive carbon deposition.

Fractionation of Tasmanite Shale Petrol.

Although the petrol is a mixture of so many hydrocarbons of several series and the hope of any considerable separation of the various compounds is small, yet a fractionation was carried out on one sample as an exploratory test.

The sample available at the time was one deficient in the lower boiling oils, which was somewhat of an advantage from an experimental point of view, as the vapour losses of oil were thus minimised.

It was the fraction previously mentioned and distilled from the first sample of commercial oil from the Tasmanite Shale Oil Co. It distilled over principally between 120°C and 185°C. It had been treated with sodium hydroxide solution for removal of hydrogen sulphide and acid oils and then with 10% sulphuric acid for removal of basic oils, the refining losses being 5.9% and 1.5% of the original fraction respectively.

Before proceeding with the fractionation, the oil, which had stood six months after the previously mentioned treatments, was given two successive 1% treatments with 95% sulphuric acid followed by soda and water wash. The volume was reduced from 1230 m.l. to 1165 m.l. The loss corresponds to 2.64% per 1% acid. The washed oil was .810 specific gravity.

It was distilled in three lots of approximately 400 m.l. with a 12 bulb rectifying column and fractions collected every 10°C.

All the fractions obtained were then re-run in the usual manner and distillates passed up and down the house, to use the terminology of the Pattinson desilverising process.

Seven series of distillations were carried out and then the two first, - 80°C. and 80°C.- 90°C., and the fractions from the 200°C - 210°C. one and over were too small to redistil, as the limits of the apparatus had been reached.

The charging of the fractions into the distilling flask was done through a special small side tube, so as to minimise loss of vapour, and the distillates were received direct into the appropriate bottles which had vertical paper scales pasted on. On this scale the level of the surface of the oil was marked each time, in order to keep check of the increase or decrease in the amount of fraction.

After 8 complete series of fractionations, the volumes, specific gravities and sulphur content by the lamp method were determined. A Richardson lamp was not available, so that a simple form of lamp was used and the sootiness of the flame with these highly unsaturated oils eliminated by burning the oil mixed with sufficient sulphur-free alcohol to dissolve it. The lighter fractions burnt satisfactorily mixed in the proportion of 1 oil : 2 alcohol, while the heavier fractions required more alcohol to dissolve them. As will be seen from the following table, the volumes, specific gravities and sulphur contents were by no means uniform in their variation, showing that a separation of constituents had taken place, at least to a partial extent.

Result after 8 Fractionations.

Fraction.	Sp. Gr.	Volume.	Grams.	% Sulphur.
- 80°C.	.745	18.5 m.l.	13.8	1.23
80°C.- 90°C.	.766	14.0	10.7	1.63
90°C.-100°C.	.755	31.0	23.4	1.95
100°C.-110°C.	.781	68.5	53.5	3.30
110°C.-120°C.	.792	83.0	65.7	3.62
120°C.-130°C.	.778	100.0	77.8	2.74
130°C.-140°C.	.793	102.0	80.9	3.60
140°C.-150°C.	.797	138.0	110.0	3.32
150°C.-160°C.	.798	86.5	69.0	3.26
160°C.-170°C.	.814	95.0	77.2	3.90
170°C.-180°C.	.812	95.0	77.1	3.18
180°C.-190°C.	.822	55.5	45.6	3.15
190°C.-200°C.	.827	48.5	40.1	2.67
200°C.-210°C.	.844	32.0	27.0	2.94
210°C.-220°C.	.857	25.0	21.4	3.12
220°C.-230°C.	.860	10.0	8.6	N.D.
+ 230°C.	.927	106.0	98.3	N.D.
Totals		1108.5	900.1	
Original		1165	945	

After the above results were obtained, the fractionation was continued for three more series and then, as the volumes did not show much change, sulphurs were determined on the 130°-140°C, and on the 160°C.-170°C. fractions. These ran 3.60% and 3.99%, showing that little change was taking place and that with 10°C. intervals not much was to be gained by continuing. It will be observed that up to the end of the 8th. fractionation 56 m.l. of oil had been lost, which is not excessive considering the amount of manipulation. It is regretted that 5°C. intervals were not used, but the amount of work involved was too great to repeat this work without assistance.

On plotting specific gravities and sulphur contents against boiling points, the steady rise of specific gravity with increase

of boiling point is disturbed in several places. More than normal gravities are shown by the 80°C.-90°C., 100°C.-110°C., 110°C.-120°C. fractions particularly. The first of these would be largely due to benzene and thiophene, while the second two to toluene and methyl thiophene, both of which boil in this range.

The sulphur percentage shows three distinct maxima and three distinct minima. The first maximum occurs in the 110°C.-120°C., the second in the 130°C-140°C. range, and the third in the 160°C.-170°C. range. The two isomers of thiotolene or methyl thiophene boil at 113°C. and 120°C., while the four isomers of dimethyl thiophene or thioxene boil at 135°C., 136°C., 138°C. and 145°C. It is reasonable to link these three sulphur maxima with methyl, dimethyl, and trimethyl thiophene. Similarly, the sulphur minima occur in the boiling ranges of octane, nonane, decane, and undecane.

The fractionation as far as carried has therfore gathered the principal thiophene derivatives and the paraffins present into their respective boiling ranges, and indicates with considerable certainty the presence of these compounds. The absence of a maximum for thiophene itself is explainable by the fact that the crude oil from which this heavy petrol fraction was obtained contained very little of the lower boiling compounds.

After eleven fractionations the 160°C.-170°C. fraction ran 3.99%. The 93 m.l. of this fraction, which was left after sampling, was refractionated with 2°C. intervals and the portion distilling below 160°C. was later refractionated twice into two portions - 155°C. and 155°C.-160°C. The volumes obtained, together with sulphur content, are as follows:-

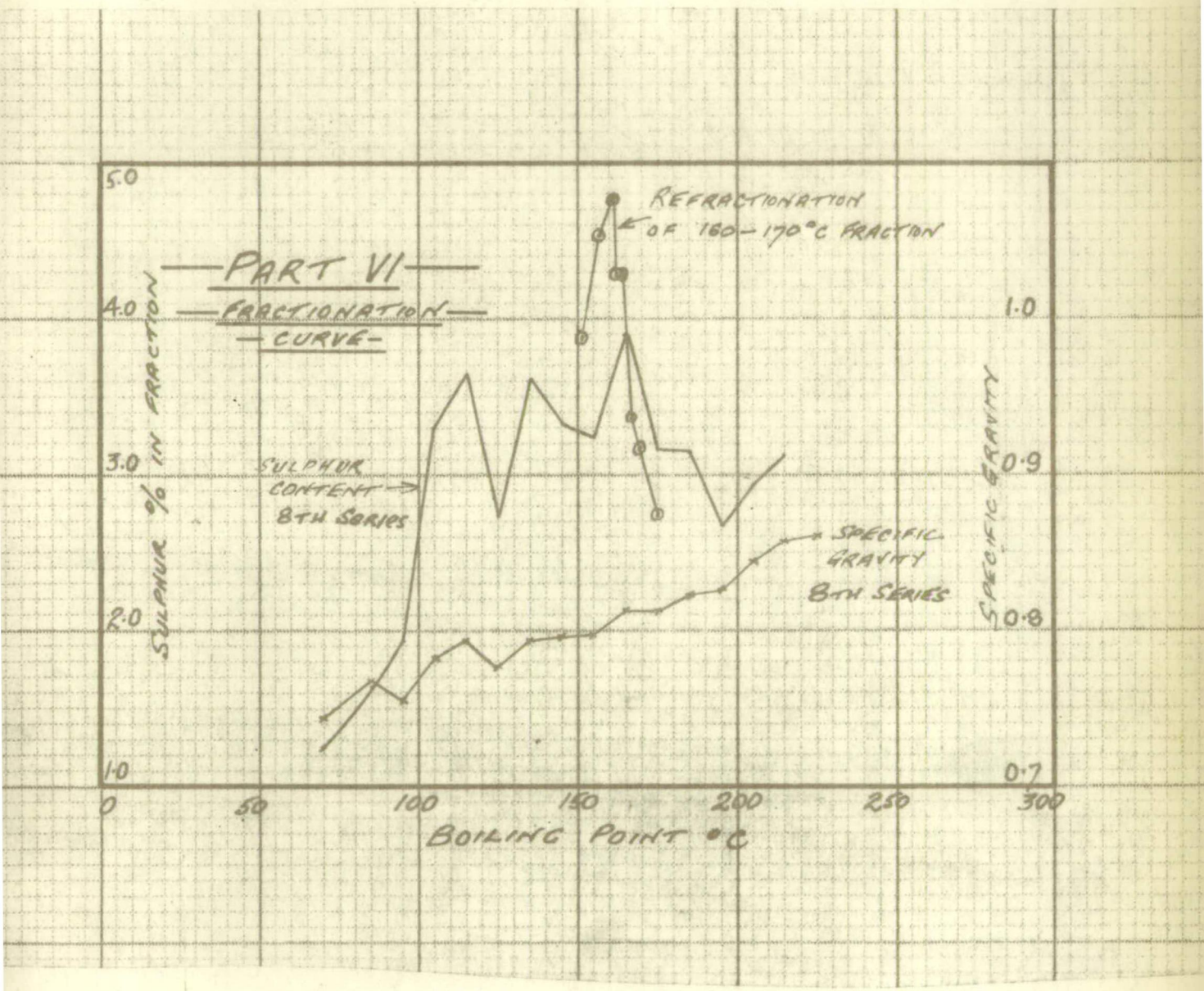
Boiling Range.	Volumes.	Sulphur content.
- 160°C.	23.3 m.l.	4.30 %
160°C.-162°C.	9.2	4.77
162°C.-164°C.	9.2	4.29
164°C.-166°C.	11.5	4.29
166°C.-168°C.	12.2	3.37
168°C.-170°C.	6.0	3.18
+ 170°C. and loss	21.6	2.72

The -160°C. portion which was separated into two portions gave results as follows:-

Range.	Volume.	Sulphur Content.
- 155°C.	7.5 m.l.	3.86 by calculation.
155°C.-160°C.	13.5 m.l.	4.55%

The refractionation with the closer temperature intervals has resulted in the increasing of the maximum to 4.77% sulphur in the

160°-162°C. fraction and on either side of this the sulphur content decreases.to the fractions containing respectively considerable quantities of nonane, boiling at 150°C., and decane, boiling at 173°C. With closer temperature intervals it is certain a better separation could be obtained and fractions prepared richer in sulphur. However, sufficient work was done to indicate with certainty the presence of the thiophene homologues in sufficiently large quantity to account for the great bulk of the sulphur content of the oil.


PART VI
FRACTIONATION
CURVE
REFRACTIONATION
OF 160–170°C FRACTION
SULPHUR
CONTENT →
8TH SERIES
SPECIFIC
GRAVITY
8TH SERIES
SULPHUR % IN FRACTION
SPECIFIC GRAVITY
BOILING POINT °C
5.0
4.0
3.0
2.0
1.0
1.0
0.9
0.8
0.7
0
50
100
150
200
250
300

PART VII.

COMPOSITION OF TASMANITE SHALE OIL DISTILLATES.

During the course of the retorting work described in Part III, the fractions from the distillation analyses were preserved and at a later date were examined to gain an idea of the hydrocarbon composition of these distillates. At the same time a range of distillates from a crude oil supplied by the Tasmanite Shale Oil Co. and a refined petrol from Mineral Oils Extraction Ltd. were similarly examined for comparative purposes. All of the crude distillates were very dark coloured from oxygen absorption and standing a good time, and were in some cases very difficult to separate from the refining or extracting acid. It is not thought, however, that the standing and colouring has materially affected the results.

This particular phase of the work has been greatly handicapped by the lack of available in formation in Tasmania, e.g., there are no volumes of the Journal of the Institution of Petroleum Technologists, or similar publications, available here, and the large amount of work that has already been done in the other parts of the world on the composition of petroleum distillates was not available to any great and useful extent. On this account, this part of the work is lacking in completeness, but a useful amount of work has been carried out and is given below.

It is quite apparent that it is very difficult to distinguish sharply between the various classes of hydrocarbons and that there exist many hydrocarbons possessing the characteristics of two classes, e.g., certain derivatives of cyclohexane and aromatics. It is thus impossible to place the hydrocarbons present in a petroleum distillate into watertight divisions, but, at the same time, it is possible by using a variety of time consuming methods to gain a very close idea of the hydrocarbons present. Such information may not necessarily be so valuable to the refiner nor to the user of the product as it is satisfying to the chemist who has unravelled the tangle.

As sulphuric acid is still the cheapest refining agent in most cases this work has been principally confined to an investigation of the action of concentrations of sulphuric acid varying from 10% to 98% on the distillates, together with the determination of the aniline points of the paraffinic residue so that the presence of naphthenes might be detected and their amount determined.

The following successive treatments of the oils were adopted, the residual oil volume being measured after each treatment.

1. Removal of hydrogen sulphide and acidic oils soluble in 10% sodium hydroxide solution.

2. Removal of basic oils by preferential solution with 10-18% sulphuric acid.

3. Removal of unsaturateds (olefines etc.) by extraction with two volumes of sulphuric acid per volume of oil at room temperature. The acid-oil mixture rose 10-20°C. above room temperature, but would not exceed 35°C. in any case.
   The exact strengths of acid used were 80% and 83.8%, the latter being somewhat above the 83% which is stated to have little action on the aromatics. If the results are desired on 83% acid proportional interpolation is sufficiently accurate.

4. Removal of aromatics and thiophenes by extraction with acid of 97.8% strength, two volumes of acid per volume of oil in one series and three volumes of acid in another.
   The distillates from the commercial oil were also treated with two volumes of 95% acid in a third series.

5. The residual oil was washed with sodium hydroxide solution to remove all acid, well settled and separated. The oil was then dried by standing over solid calcium chloride and sodium hydroxide for some days before determining the aniline point. The aniline used was pure and freshly redistilled with the first aqueous distillate discarded. The main portion of the distillate was used and kept dry over solid potassium carbonate.

Care was taken to keep evaporation losses low in the work on the lighter distillates by using separatory funnels of suitable size and keeping the vapour space small. However, in the handling of these some small losses unavoidably occur. Another difficulty

was that the oil surface could not be seen in many cases, owing to the colour of the oil, especially after 80% acid washing. In the case of the heavier distillates, the thicker oil film left on the separatory funnel inner surface introduces another error. However, wet vessel losses were kept low by using the same separatory funnel and graduate throughout and allowing ample time for drainage. In view of these difficulties, measurement of the oil volumes is not reliable to closer than .5 m.l. or to 0.5%.

A certain amount of further explanation is also necessary. In the sodium hydroxide treatment, no difficulty is experienced in separating the aqueous layer from the oil with distillates under 200°C. Above this temperature, the shaking together of the caustic solution and the oil produces on settlement a three layer system. The lower aqueous layer is easily separated, but separating this from the oil proper is a tarry or oily layer of higher viscosity than the oil but practically indistinguishable from the oil. In the fraction 250°C-300°C. the sum of this tarry layer and the oil is several percent over the original oil started with, indicating that water had been taken up. This dark tarry layer was run off in the case of those fractions which produced it and counted as soluble in the sodium hydroxide. Whether there is an appreciable amount of pure hydrocarbons dissolved in this layer is not known, but it is probable that some oil escapes in this way.

Likewise treatment with 18% sulphuric acid produces in the higher boiling distillates a three layer system, the intermediate layer of dark colour and high viscosity consisting of polymerised gum forming unsaturateds. Acid of 10% strength has less polymerising power and in both cases the effect increases with the boiling point of the oil. In those cases in which this layer was produced, it was retained with the oil and its volume measured with it, as it more properly belongs to the unsaturated portion and not to to the basic oils. Treatment with 80% and more noticeably even with 83.8% acid produces this dark layer of polymerised and sulphonated unsaturated hydrocarbons. In the case of the higher boiling distillates its volume was relatively considerable. Again, it is a doubtful point if much of the residual oil is soluble in this layer. It was run off after the acid treatment and counted with the unsaturateds. Properly speaking, the oil should be distilled at this stage to get rid of the polymerised unsaturateds dissolved in the oil, but the smallness of the quantity of oil available did not allow this refinement.

Treatment of the now unsaturated-free oil with 98% acid only produces two layers and separation in this case is not so difficult, especially as the oil is lightened in colour by the strong acid washing.

The oils emulsify badly with water washing, as the sulphonated compounds, soluble to some extent in the oil, are very powerful emulsifying agents. After the final measurement of the oil which was made in the acid state the oil was transferred to a clean separatory funnel containing sodium hydroxide solution of about 20% strength and washed with this. After 24 hours settlement and separation of the caustic layer, the oil was transferred to the drying bottle.

In all cases treatment with the various reagents was made by shaking thoroughly at intervals for one to two hours and settlement effected by 24 hours standing.

The acid strengths were determined by specific gravity bottle and correction made for temperature. These values were in very good agreement with the values obtained by volumetric analysis using carefully calibrated apparatus.

In all cases the acid strengths are given to 0.1%, which was the limit of accuracy of the method used.

The acid used to remove the aromatics was 97.8% and this was the most concentrated available. 98.8% is frequently specified as being necessary, but by using 3 volumes of 97.8% acid the removal of aromatics is practically complete, so that a further treatment with 5 volumes of acid does not raise the aniline point.

The results obtained are shown in summarised form in the following tables.

Distillates from Laboratory Produced Crudes.

The volume used in each case was 100 m.l.

A. refers to removal of unsaturated hydrocarbons with 2 volumes of 80% sulphuric acid and aromatics etc. with 2 volumes of 97.8% acid.

B. refers to removal of unsaturated hydrocarbons with 2 volumes of 83.8% sulphuric acid and aromatics etc. with 3 volumes of 97.8% acid.

Fraction		70°C-150°C.	150°C.-200°C.	200°C.-250°C.	250°C.-300°C.
Sp. Gr.		.767	.832	.876	.912
Saturation % 3 vols.97.8% acid		56	46	38	28
Average % of crude oil		12.0	9.8	10.5	12.6
Loss to Sodium hydroxide-acid oils		2.0%	4.0%	5.8%	10.0%
Loss to 18% sulphuric acid - basic oils		1.5%	3.5%	4.2%	4.0%
Unsaturateds	A	26.5	19.5	16.0	27.0
	B	25.0	19.5	30.0	32.0
Aromatics & thiophenes	A	21.0	35.0	48.0	41.0
	B	22.5	36.0	34.0	38.0
Paraffins & Naphthenes	A	49.0	38.0	26.0	18.0
	B	49.0	37.0	26.0	16.0
Aniline point of paraffins & naphthenes	A	58.3°C.	69.5°C.	75.0°C.	82.5°C.
	B	65.3°C.	71.0°C.	76.5°C.	86.0°C.
Aniline point of paraffins & naphthenes after further 5 vols. of acid.	B	66.0°C.	70.5°C.	78.0°C.	86.0°C.

In general, more weight is to be attached to series B results, as they were obtained using the results of the experience on series A. For example, in the 70°C.-150°C. fraction, series B, the same amount of paraffins and naphthenes was obtained as in series A, in spite of using 3 volumes of 97.8% acid and a higher aniline point was obtained. This was due to eliminating much of the evaporation loss by more careful handling. In series B the actual measured volumes of the three heaviest fractions were 0.5 m.l. below those given and were increased to the nearest whole number to allow for the wet vessel loss which adversely affects these fractions. The residual paraffins and naphthenes from series B of volumes 20 m.l., 20 m.l., 10 m.l., and 8.5 m.l., respectively, were treated with 5 volumes of 97.8% acid to see if the aniline points could be raised by further removal of aromatics, if any. The recovered oil volumes were 19.3, 19.4, 9.6, and 8.2, respectively, which, allowing for the wetting of the funnel, shows very little removal of oil. The white acid used showed a slight colour change on agitation from a deep yellow to a light brown, according to boiling point. It may be accepted therefore that, while 2 volumes of 98% acid is barely sufficient to remove all the aromatics, 3 volumes is sufficient and will give higher aniline points than two

volume treatment. Further acid treatment then has no appreciable effect on the aniline point.

With regard to using 80% and 83.8% acid to determine unsaturateds, there is little difference in the first two fractions and not a great difference in the last fraction. In the third fraction the 83.8% acid makes the unsaturateds nearly double compared with 80% acid. It is difficult to understand this difference, but it does not seem due to lack of care as all fractions had the same treatment as regards agitation etc. It may be that in this boiling range there are unsaturated hydrocarbons very easily polymerised by 83.8% acid which are relatively unaffected by 80% acid. It was definitely noticed that the dark intermediate polymerised layer was very considerable in this fraction.

As regards the relative amounts of paraffins and naphthenes present in the residual oil, there is some degree of uncertainty. The data are as follows, assuming that the measured oil volume after treatment with 3 volumes of acid in series B possesses the higher aniline points found.

Average Boiling range of fraction. (Midpoint).	Aniline Point.	Aniline point of pure paraffins - interpolated.
120°C.	66.0°C.	70.5
175°C.	70.5°C.	78.0
225°C.	78.0°C.	87.6
275°C.	86.0°C.	97.5

The aniline points of the pure paraffins were obtained by interpolation from the values given by Carpenter, "Composition of Petroleum Fractions", Journal of the Institution of Petroleum Technologists, Vol. 14, 1928, pp. 446-476. In the same volume there is an article by Garner on the determination of aromatic, olefine, naphthene and paraffin hydrocarbons. In this article there are some graphs given (figure 2) to determine the proportions of naphthenes and paraffins in the aromatic and olefine free petrol. According to these graphs, the first fraction given above consists of 24% naphthenes and 76% paraffins. This corresponds closely to an aniline point depression of .2°C. for each 1% of naphthenes present in the naphthene paraffin mixture.

Carpenter (op. cit.) considers from his work that in the spirit and kerosene ranges 1% of naphthene depresses the aniline point 0.2°C., with the exception of certain complex polynuclear naphthenes in the region of 300°C. boiling points. Other workers, such as

Ormandy and Craven, confirm this view. It is commonly stated that the depression per 1% of naphthene is 0.3°C. and even 0.4°C. is sometimes given.

For purposes of comparison, the percentages of naphthenes will be worked out on the basis of both 0.2°C. and 0.3°C. depression per per cent. naphthenes.

Fraction. Average Boiling Point.	0.2°C. basis.		0.3°C. basis.	
	% naphthenes.	% paraffins.	% naphthenes.	% paraffins.
120°C.	22	78	15	85
175°C.	38	62	25	75
225°C.	48	52	32	68
275°C.	58	42	38	62

The composition of the original crude fractions can now be given, taking values for the unsaturateds given by 83.8% acid and assuming that the 0.2°C. basis is the correct one for the naphthenes.

Distillate.	70°C.-150°C.	150°C.-200°C.	200°C.-250°C.	250°C.-300°C.
Acidic oils	2.0%	4.0%	5.8%	10.0%
Basic oils	1.5	3.5	4.2	4.0
Unsaturateds	25.0	19.5	30.0	32.0
Aromatics & thiophenes	22.5	36.0	34.0	38.0
Naphthenes	11.0	14.0	12.5	9.0
Paraffins	38.0	23.0	13.5	7.0
	100.0	100.0	100.0	100.0

Figures in most cases have been rounded off to the nearest 0.5%. If 0.3°C. be accepted for the naphthene factor, the naphthenes are respectively 7.0%, 9.0%, 8.5%, 6.0%, and the paraffins 42.0%, 28.0%, 17.5%, 10.0%.

Whatever basis is acceptable, it will be observed that the paraffin content of the oil drops rapidly with increase of boiling point, whereas naphthenes have a much more even tenor and are at a maximum in the 150°-200°C. fraction.

Comparative work on Commercial Oils.

The work on the M.O.E.L. refined petrol and three distillates from the Tasmanite Shale Oil Company's crude may be summarised in the same way as was done for laboratory produced oils.

The volume used in each case was 100 m.l.

A. refers to removal of unsaturated hydrocarbons with 2 volumes of 80% sulphuric acid and aromatics etc. with 2 volumes of 95.1% acid.

B. Refers to removal of unsaturated hydrocarbons with 2 volumes of 80% sulphuric acid which in the case of the 175°C.-225°C. and 225°C.-275°C. fractions was repeated. The increased removal of unsaturateds being 1.0% and 1.5% of the original oil volume. The results are given in these two instances for the 4 volumes of 80% acid. The removal of aromatics was carried out with 2 volumes of 97.5% acid.

C. Refers to removal of unsaturateds with 2 volumes of 83.8% acid and aromatics etc. with 3 volumes of 97.8% acid.

Distillate.		M.O.E.L. Refined Petrol.	T. S. O. Co. distillates. 120°C-175°C.	175°C.-225°C.	225°C.-275°C.
Sp.Gr.		.771	.799	.849	.899
Saturation %					
3 vols.95.1% acid			64%	57%	48%
3 vols.97.8% acid		66.0	56%	50%	38%
Average % of crude		-			
Loss to sodium hydroxide - acid oils		-	2.9%	5.0%	6.7%
Loss to 10% sulphuric acid - basic oils		-	1.4%	2.5%	4.8%
Unsaturateds	A	8.0	16.3	17.1	17.3
	B	n.d.	17.2	17.6	18.6
	C	18.0	23.0	22.2	24.8
Aromatics & Thiophenes	A	24.0	23.0	25.5	35.0
	B	n.d.	29.5	32.4	43.4
	C	24.0	23.6	28.7	37.0
Paraffins & Naphthenes	A	68.0	56.4	49.9	36.2
	B	n.d.	48.6	42.5	26.5
	C	58.0	49.1	41.6	26.7
Aniline point of Residual oil	A	52°C.	53.5°C.	57.5°C.	64.5°C.
	B	n.d.	n.d.	n.d.	n.d.
	C	58.5°C.	62°C.	65.5°C.	77.5°C.
Aniline pts. after further 5 vols.of 97.8 sulphuric acid	C	60.5°C.	63.8°C.	68°C.	80.8°C.
Average boiling pt. of distillate		124°C.	148°C.	200°C.	250°C.

In the last treatment (5 volumes acid) of the paraffin fraction a little loss of oil took place as judged by the darkening of the acid. It is difficult to determine the actual loss as the wet vessel losses are somewhat variable. 20 m.l. of each of the above were taken and in order from left to right the measured residual volumes were 19.2, 19.1, 19.1, and 18.3. These are all somewhat lower - the last definitely so - than in the cases of the laboratory distillates, indicating that a small amount of aromatic hydrocarbons was removed in each case. The volumes of the paraffins and naphthenes as given opposite letter C are thus somewhat high but, allowing for the wetting of the funnels in the 5 volume acid treatment, would not be reduced by much more than 1% of the original fraction taken by complete removal of aromatics. In the following discussion it will be assumed that the volumes given opposite C possess the higher aniline points found. The error involved is comparatively small.

The data for the determination of the proportion of naphthenes present is as follows:-

Fraction - average boiling range.	Aniline point of mixture.	Aniline point of corresponding paraffins (interpolated).
124°C.	60.5°C.	72°C.
148°C.	63.8	73.8
200°C.	68.0	82.5
250°C.	80.8	92.6

On a 0.2°C. unit depression the mixtures contain in order 57%, 50%, 72% and 59% of naphthenes. On the 0.3°C. unit depression the percentages are 37, 33.4, 48, and 39%, respectively. If Figure 2 in Garner's article be accepted, then the first one consists of exactly 50% paraffins and 50% naphthenes.

The composition of these distillates may now be given, assuming that 83.8% acid gives the more correct measure of the unsaturateds and that 0.2°C. is the unit depression of the aniline point of the paraffin naphthene mixture.

Distillate.	M.O.E.L. Refined.	T. S.,O. Co.' oil. 120°C-175°C.	175°C-225°C.	225°C-275°C.
Acidid oils	-	2.9	5.0	6.7
Basic oils	-	1.4	2.5	4.8
Unsaturateds	18.0%	23.0	22.2	24.8
Aromatics-thiophenes	24.0	23.7	28.7	37.0
Naphthenes	33.0	24.5	30.0	15.5
Paraffins	25.0	24.5	11.6	11.2

If the 0.3°C. be accepted as the unit depression of the aniline point, the naphthenes and paraffins are respectively

Naphthenes	21.5	16.5	20.0	10.5
Paraffins	36.5	32.5	21.6	16.2

Discussion of results on laboratory and commercial distillates.

Before entering on a discussion of the foregoing results, it is instructive to quote from Garner, "Analysis of Cracked Spirits", Journal of Inst. of Pet. Technologists, Vol. 14, 1928, pp. 695-715.

"Aromatic hydrocarbons behave as though they were slightly unsaturated and olefines vary considerably in their reactiveness to different reagents, and so far no reagent has been discovered that will completely remove olefines without at the same time removing also at least part of the aromatic hydrocarbons present. We have investigated a number of reagents of different types such as bromine, hypochlorous acid, potassium permanganate solution, and stannic chloride, without finding one suitable for analytic purposes.

.....

"The low reactivity of the higher olefines, and the instability of the addition compounds which they form, render the separation of olefines from aromatic hydrocarbons very difficult.

"Sulphuric acid has been used as an approximate method for the estimation of olefines in cracked spirit although it is recognised that the resulting treated oil contains polymers, so that the actual olefine content is higher than that measured by loss in volume. Attempts have been made to determine the proportion of polymers by distillation to a lower end-point than that of the cracked spirit. This method is used in the approximate method of analysis of Egloff & Morrell (J. Ind. Eng. Chem., 1926, 18, 354), but does not give accurate results because the polymers from the lowest boiling olefines present distil below 150°C., which is much below the end-point of the average cracked gasoline. A further objection to the use of sulphuric acid, where aromatic hydrocarbons are also estimated, is that this reagent not only removes olefines, but also aromatics (Garner, J. Inst. Pet. Tech., 1926, 12, 66; Brame, Ibid, 221). Attempts have been made by Brame (J. Inst. Pet. Tech. 1926,,12, 221), with 85 per cent. and 88 per cent. sulphuric acid, but it was found that even with these dilutions, condensation of olefines and aromatic hydrocarbons take place in accordance with the reaction discovered by Brochet (Bull. Soc. Chim., 1893, 9, 867), thus with the 85 per cent. sulphuric acid about 30 per cent. of the aromatic hydrocarbons used was found to be removed. Ormandy in a number of recent papers has also shown the complicated nature of the reaction between sulphuric acid and cracked spirit.

"Even with 98-100 per cent. sulphuric acid, as used in the Institution of Petroleum Technologists Standard Method for the estimation of aromatic hydrocarbons (which is limited to the analysis of straight-run petrols), the treated portion of a cracked spirit does not correspond with the paraffin and naphthene content of the spirit; removal of the olefines and aromatic hydrocarbons and their reaction products is not completely effected even with this concentration of acid. It is known that more highly concentrated acid will attack the naphthenes present in gasolines.

.....

"With sulphuric acid and cracked spirit two reactions occur:-

(1) Polymerisation, giving products of higher specific gravity and aniline point than the original spirit.

(2) Condensation of olefines and aromatic hydrocarbons to give products of higher specific gravity and aniline point than the original spirit.

The products of these reactions are not completely removed by the sulphuric acid treatment, with the result that the specific gravity of the acid-treated spirit is always higher than that of the paraffin and naphthene portion of the cracked spirit, but the aniline point is sometimes higher and sometimes lower after the treatment, depending whether the aromatic hydrocarbon content is high or low.

There are thus two fundamental sources of errors in the sulphuric acid method for the analysis of cracked spirits:-

(1) Olefines and aromatic hydrocarbons are removed and simultaneously addition products formed, so that the loss in volume does not give a true indication of the olefine and aromatic hydrocarbon content.

(2) The treated portion of the cracked spirit is not the same as the paraffin and naphthene portion of the cracked spirit, with the result that the properties of this acid-treated spirit cannot be used for the estimation of the paraffin and naphthene contents."

The limitations of the sulphuric acid method of analysis are fairly fully pointed out in the above given extract, nevertheless, the method has its uses, as sulphuric acid is in general the commonest refining agent. The problem of estimating or determining the composition of cracked spirit is closely related to the same problem as regards shale distillates,as shale oil is really a distillate formed by the cracking of a high boiling bituminous stock. The two problems have therefore much in common. It was not possible single-handed to investigate or apply all of the known methods of analysis, as so much weighty criticism has been launched against the majority of them. For future investigation, if warranted, additional work on the lines given by Garner would be very interesting and instructive. On account of time limitation, the sulphuric acid method was adopted, as it is nearly related to practical oil refining and gives information as regards refining in a very direct way.

It is frankly admitted that the analysis of such a complex mixture as a shale oil distillate by the foregoing method does not possess the exactness that one would prefer to see, but the difficulty lies in the complexity of the combinations of carbon and hydrogen. While distinct types of compounds are clearly recognisable, there are so many which share the characteristics of two types at least, and the placing of such a hybrid into a certain class depends very much on the reagent chosen for separation.

It will be noticed on looking over the results that different percentages of unsaturated hydrocarbons are obtained using 80% acid and 83.8% acid. It is possible that 83.8% was a little too concentrated, but the greater proportion of unsaturateds obtained using it would appear more in keeping with the general nature of the oil. In certain cases the treatment with 80% acid was repeated, but comparatively little further oil was removed. It would appear more correct to take the figures obtained using 83.8% acid, although they may be slightly high. In the case of the refined shale petrol, the stronger acid removed over twice as much as the weaker acid, but from the general behaviour of this petrol as regards gum formation, bromine absorption etc. the higher value would certainly appear the more correct one.

In the case of the commercial distillates, on comparing series A and C the percentages of aromatics plus thiophenes are much the same as the incomplete removal of aromatics from the paraffins in series A compensated for the incomplete removal of the unsaturateds.

Another difficulty that arises is whether to accept 0.2°C. or 0.3°C. as the unit depression figure for determining the proportion of naphthenes present. By accepting the lower figure, the proportion of naphthenes is made larger than in the other case, but most recent comments and statements appear to lean to the 0.2°C. figure. In any case, the separated naphthene-paraffin mixture after washing thoroughly was decidedly naphthenic in smell, indicating that some considerable proportion of naphthenes was present.

The general results are presented in the accompanying graph. By inspection of this and reference to the tables of compositions given it will be seen that

1. The acid oil content extractable by caustic soda solution is practically the same for both commercial and laboratory produced oils and it increases as a straight line function of the boiling point.

2. The basic oil content is much the same in the two cases and likewise increases with the boiling point.

3. The unsaturated content in both oils is much the same in the petrol range, but in the kerosene range and higher the unsaturated content is greater in the laboratory produced oils.

4. The aromatic and thiophene homologue content is less in the case of the commercial oil with distillates boiling under 200°C., but over 225°C. becomes much the same.

5 The commercial oil is definitely higher than the laboratory produced oil in naphthenes and paraffins. The pure paraffin content using the 0.3°C. unit depression of the aniline point is very closely the same, but on the 0.2°C. basis the laboratory oils are higher in paraffin content. As the commercial oil was severely vapour phase cracked, this would be expected and it probably indicates that the 0.2°C. basis is the more correct.

One point that needs bearing in mind is that condensation of the lower boiling portions of the commercial oil was poor and this affects somewhat the lower boiling end of the graph. In general, there is considerable similarity between the distillates from laboratory crudes where vapour phase cracking was at a minimum and the distillates from a rather severely vapour phase cracked commercial oil. Average commercial retorting would produce an oil about midway in composition between the two. It would seem that the oil retains its principal characteristics under very varying treatment and short of destructive vapour phase cracking, as in Runs 30 and 31 (Part III), retains these characteristics over a wide range of treatment. It is therefore possible to discuss Tasmanite shale oil generally irrespective of the retorting process used.

The outstanding fact is that the true paraffin content of even the low boiling distillates is low - considerably less than half - and as the limit of the kerosene range is reached, say 275°C., the true paraffin content is in the vicinity of 10% or less, while at 300°C. the total of naphthenes + paraffins is in the region of 10% only.

As a source of lubricating oils or waxes, Tasmanite shale oil is very poor and of no commercial value. For the same reasons, it is economically impossible to make a lighting kerosene, as even a naphthenic kerosene has relatively poor illuminating value.

Apart from the creosote, basic oils, bituminous road oil, and bitumen, it would appear that Tasmanite shale oil is only suited for fuel purposes, either to be burnt direct as a fuel oil, or in the form of certain distillates.

Excluding for the moment the acid and basic oils, the remainder of the oil is very approximately evenly divided between unsaturateds, aromatic and thiophene homologues, naphthenes, and paraffins. The last named preponderate in the lower boiling fractions and decrease with rise of boiling point, but in most distillates are well represented and their place in the higher boiling distillates is taken by unsaturateds and aromatics. All these distillates in the relatively crude state have excellent combustion characteristics, but the more they are treated and refined to produce products similar to those on the market, the poorer they become in performance.

The bulk of the sulphur is contained in the aromatic and thiophene portion and these are so strongly entrenched behind the unsaturated hydrocarbon content as to make it almost impossible in commercial refining to get at the sulphur containing compounds. In order to completely remove the sulphur compounds, nearly all the unsaturateds and much, if not nearly all, of the aromatics must be also removed. The work outlined in this section also shows that relatively weak acid of 84% strength will remove a considerable fraction of the oil. The use of oleum with its apparently greater success is also explained, as its superior sulphonating power enables it to sulphonate whatever comes in its way, so that it sulphonates thiophenes in the presence of unsaturateds more successfully than, say, 93% acid, which might be commonly used and which preferentially attacks the unsaturateds. It may be accepted that sulphuric acid (excluding oleum which has not been investigated) refining for taking out the sulphur is commercially unsuitable, as it takes out the compounds which contribute most to the anti-knock qualities of the fuel.

The writer personally used shale petrol for about 600 miles in a car (1928 model A Ford) without any special tuning or adjustments and has noted the decreased anti-pinking quality of the petrol with increased refining. With a petrol just sufficiently refined to be gum stable for a month or two, it was impossible to make the engine knock even by giving full throttle with full advanced spark on a steep hill at low speeds. The petrol gave the engine steam engine like qualities and the mileage rose on the same type of running from 22 to 25 miles per gallon, though portion of this would be due to the extra weight per gallon of the high gravity shale petrol. This petrol, apart from its rather pronounced smell and sulphurous exhaust, was the best performing petrol ever used in an engine rather given to pinking.

As refining technique improved at the works and a more refined spirit was turned out, the performance fell off somewhat and the most refined shale spirit used behaved much like a standard No. 2 petrol - "Imperial", and in general running gave very similar results.

The M.O.E.L. refined petrol on which the work reported in this section was done was also given a road test on an accurately measured quantity.

The petrol contained a little over 2% sulphur and had a pronounced shale petrol odour. It was barely gum stable, indicating that refining was only just sufficient and not excessive. There was no trouble in starting with it, though the lower boiling fractions were somewhat deficient. The distillation analysis was as follows, using the standard apparatus.

Initial boiling point (first drop)	70°C.
10% over	96°C.
20	104
30	110
40	117
50	124
60	130.5
70	138.5
80	149.5
90	167.0
98.5 & end point	201

On a fairly level run, Hobart to New Norfolk, with a Ford Model A Sedan with 5 passengers, the car did 30.3 miles per gallon for the return journey, and for a 7.5 mile run on the Huon road and climbing 1400 feet the mileage per gallon was 16.4. The first of these results is fully 20% better than on standard petrol, as 25 to 26 miles per gallon represents the maximum performance of this car and 23 to 24 miles per gallon an average one on a level road. The shale petrol has thus an excellent road performance.

On the hilly run this sample of petrol was somewhat inferior to "Shell Imperial" in its tendency to pink, though it should be stated that the particular engine is rather given to pinking when in average condition. In this case it had done 8,000 miles without being decarbonised and no adjustments were made to the carburettor or ignition. Probably the 16.4 miles per gallon is good mileage for the uphill road, as petrol consumption per mile is nearly doubled when the engine is all out on top gear.

The exhaust gases, however, were markedly sulphurous and, apart from the sulphur dioxide, contained a small amount of unburned products of quite objectionable smell.

The rather glowing reports one sometimes hears of shale petrol are thus largely true, with a certain qualification. A mileage increase of 15% is not an exaggerated figure and the road performance is excellent, but these qualities are most found in the less refined petrol and the treatments necessary to produce a product nearer to standard quality as at present sold in Australia result in the partial loss of the compounds which confer these desirable properties.

Similar remarks apply to the power kerosene, and in a partially refined state it has a very good engine performance. The rather low content of paraffins and high aromatic thiophene and unsaturated content combine to give a relatively light distillate which shows an excellent performance in a compression ignition engine. The particular sample referred to was a distillate of .870 specific gravity, boiling over a range of 150°C. to 340°C., with 90% over at 295°C. and a mid point of approximately 230°C.,and sold as a power kerosene. It contained 3.5%

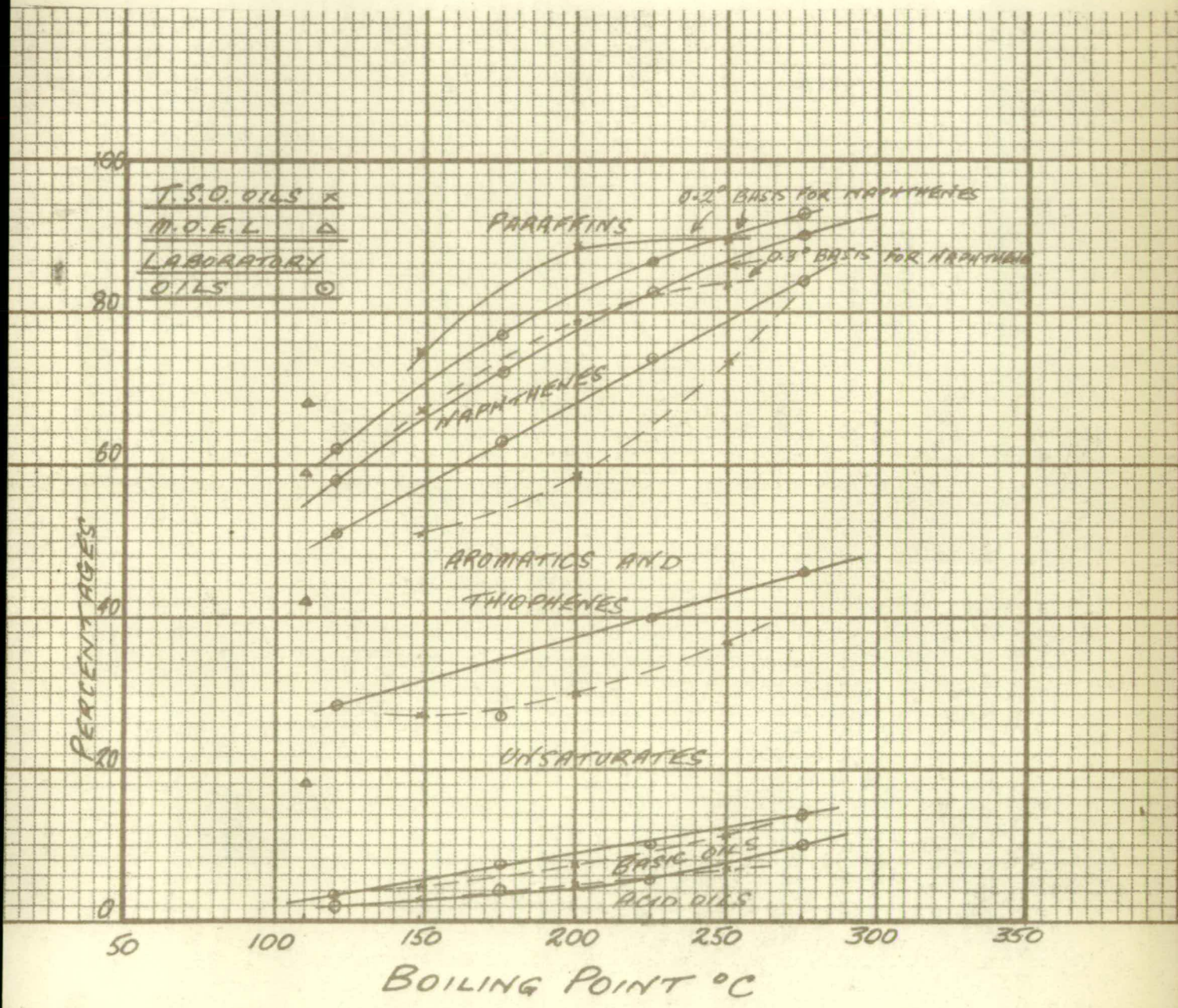
of sulphur and, as this would very largely be thiophenic, the proportion of thiophene homologues present would be considerable. This distillate ran perfectly in a compression ignition engine with 12 to 1 compression ratio. No knocking or detonation occurred and the engine gave a steady output of 26 to 27 b.h.p., whereas with a standard diesel oil which seemed to suit the engine best about 19 b.h.p. was the maximum output. The way the engine would keep up its revolutions with heavy breaking when running on the shale kerosene was remarkable. Indicator work showed that the burning of the injected oil was so steady as to maintain a constant high pressure during the early part of the power stroke, thus giving a relatively high mean effective pressure.

If no attempt is made to remove much of the sulphur from Tasmanite shale oil distillates, but refining simply carried to the point of eliminating corrosive compounds and gum forming hydrocarbons and in some cases coloured compounds, then the partly refined products have excellent characteristics as internal combustion motor fuels. Further refining beyond this point only tends to reduce engine or road performance.

As regards refining losses likely to be encountered in the refining processes, they must of necessity be large and they increase with the boiling point of the distillate. It would appear to be a necessity to remove the creosote and the basic oils in all cases and then sufficient acid has to be used to polymerise gum forming compounds such as the diolefines. In order to make the spirit gum stable for several months, several percent. of acid is necessary and the total refining losses reach 20% or over for the most refinable distillates. The consumption of reagents is correspondingly large. Both of these factors make the refining very expensive compared with well petroleum distillates, or even cracked spirit.

Although not investigated in any detailed way, it would appear from work carried out that a light vapour phase cracking at about 550°C. of the oil vapours as they issue from the retort would be one of the cheapest ways to reduce refining costs and losses, while, at the same time, a larger proportion of the more valuable lower boiling oils is produced.

In view of the work reported in this section, it may be said without fear of contradiction that Tasmanite shale oil distillates are very difficult to refine and thus entail very heavy refining losses and costs. Further, when these heavy refining losses and costs have been incurred, the refined oil is far higher in sulphur than all present day accepted standards. Compared with well petroleum distillates they appear hopeless from a commercial point of view, and, while well petroleum is so abundant and coal hydrogenation is steadily progressing, the utilisation of oil of this type seems practically limited to emergency conditions.



PART VII OIL COMPOSITION DIAGRAM

PART VIII.

GENERAL REVIEW OF TASMANIAN SHALE POSITION, SEPTEMBER 1933.

Grade and Quantity of Shale available.

The general characteristics and geological occurrence of Tasmanite oil shale in the North West of Tasmania is covered by the Mines Department geological reports to which reference can be made, such as Tasmanian Geological Survey Bulletin, Mineral Resources, No. 8, "The Oil Shale Resources of Tasmania" by A. McIntosh Reid, 1924.

Although in this publication the actual reserve is given as 10,000,000 tons and the probable reserve as 27,000,000 tons, the shale deposits have been frequently spoken of as being of the order of 40 to 50 million tons. Likewise the general impression has been that all the shale would yield an average of 40 imperial gallons per ton of 2240 lbs. in commercial retorts. This figure for oil yield is too high, though the average of the top and bottom seam approaches it in some parts of the field.

In 1931 the Committee appointed by the Commonwealth Government to investigate the Tasmanite Shale Resources requested a survey of the available shale exposures for oil content and the Tasmanite Shale Oil Company's mine and the Goliath Portland Cement Company's mine were both systematically sampled and the assay oil content of the three portions of the seam determined. The results are published at length in the "Report of Tasmanian Shale Oil Investigation Committee" 1933, Government Printer, Hobart.

In this publication the partly proved shale amounts to a little over 9,000,000 tons and with possible extensions, 25,000,000 tons represents the total of the known shale resources. These figures, which are the most reliable yet obtained, give a proper idea of the extent of the deposit. It was impossible to sample one mine, so that work had necessarily to be confined to the shale in the two mines mentioned. The amount of mining work carried out during the past eight years had opened up a larger area of seam and the results have a correspondingly greater value. The complete figures are given in Table III, page 15 of the last mentioned publication, which is given below for convenience.

TABLE III.

Section of seam.	Mine.	Sulphur.	Specific Gravity.	Thickness.	Oil Yield in Gallons per ton.
		Per Cent.	Per Cent.	ft. in.	
Top shale	Goliath	2.54	2.00	2 2.99	36.3
	Tasmanite	2.78	1.90	1 10.93	44.3
Middle band	Goliath	2.52	2.50	1 2.55	7.2
	Tasmanite	2.54	2.45	1 4.20	8.6
Bottom shale	Goliath	2.77	2.10	1 8.95	29.65
	Tasmanite	3.01	2.03	1 9.48	32.7
Top and bottom shale	Goliath	2.65	2.04	3 11.95	33.3
	Tasmanite	2.20	1.96	3 8.41	38.5
Whole Seam	Goliath	2.61	2.15	5 2.50	26.22
	Tasmanite	2.77	2.09	5 0.62	29.12

It will be noted that the average assay yield of the top and bottom seam in the Tasmanite mine is 38.5 gallons per ton, and 33.3 in the Goliath mine. The whole seam average, including the middle mudstone band, is 29.1 and 26.2 gallons per ton respectively.

It is apparent that, even excluding the band, the results fall below the popularly accepted figure for oil yield, which appears to be based on picked shale - probably top seam only. When a retorting efficiency of 85-90% is borne in mind, then 30 gallons of oil per ton is nearer to the truth for commercial yields, even when the band is left in the mine. Some parts of the field would no doubt give a little more than 30 gallons per ton, but as an average round figure it is not very far out. If this figure be accepted, and it seems that in the well-known part of the field it is substantially correct, then no less than eight tons of shale must be brought out of the mine for every ton of crude oil produced. In addition, a quantity, say 1 to 2 tons, of middle band must be broken and left in the mine. It is difficult to sum up the position as to whether the middle band should be retorted or not, but the weight of evidence is in favour of leaving it behind in the mine as far as can be done. In any case, it must be broken and shifted and thus, on the average, 8 - 10 tons of shale must be broken and 8 tons retorted for every ton of crude oil. As open cut work is impossible, and the employment of coal cutting machines impracticable, the heavy handicap on the industry is realised, as mining and retorting costs alone put a value on the crude oil above present world values.

As not all the probable shale would be profitable to mine, and an appreciable portion must be left behind in mining, it is seen that the tonnage of extractable shale is not so very large and the Tasmanian shale resources as at present known are small in comparison with those of certain other countries. In addition, some of the occurrences are scattered, making the utilisation of a large central plant rather impracticable or impossible. However, in the Railton-Latrobe area there exists a tonnage of shale of the order of 10,000,000 tons, and this is in a fairly small area only a few miles from a port, so that this shale represents a definite oil reserve of value depending on its potential oil content and on the efficiency of the extraction processes.

Retorting.

In the past too much has been made of the difficulties encountered in the retorting of Tasmanite, and at the same time the very real difficulties of refining the oil have been largely passed over through ignorance of its nature.

It is readily admitted that any large scale process needs careful design of equipment in the first place and unceasing watchfulness in operation in order to secure proper results. As regards the retorting of Tasmanite shale, some of the commercial retorts were badly designed, or, in other words, designed without due regard to the fundamental principles of shale retorting. The thermal conductivity of shale is not high and, in order to raise the centre of the charge to a sufficient temperature without having an excessive wall temperature, retorts must be relatively small in the minimum dimension. A study of the development of retort coke ovens will show that, in order to secure maximum output per unit of heating surface, retort ovens have been progressively diminished in the small dimension, so that modern ovens are only 14 inches wide. An efficient shale retort needs to be very little wider than this, if any. Using a retort width of this order, shale can be economically retorted in an all-metal retort, provided a heat resisting iron or alloy is used and no attempt made to secure freak outputs by excessive driving and consequent overheating.

The employment of too wide retorts had brought in troubles which need some heat distributing agent for their solution. In the Pumpherston retort ample steam is used, which has this effect, though it is not implied that this particular retort suffers from overheating in the metal section. Attempts have been made to recirculate retort gas or producer gas, but all these lead to increased condensation difficulties. The only practical method of using a gas to distribute heat is to use steam which can be completely condensed, though due allowance has to be made for its condensation owing to its high latent heat.

Owing to the large dilution of the kerogen with mineral matter in the case of Tasmanite, retorting of this particular shale is not relatively a difficult problem, as caking is very slight with average grades of shale and the so-called carbonisation troubles of which much has been made are due to overheating, which causes excessive vapour phase cracking of the oil vapours. Relatively speaking, the retorting of Tasmanite should be as simple as such a process can be and success or failure is mostly a matter of retort design.

In this monograph, Part III, the essentials of retorting to obtain maximum yields of oil are given, but it does not follow that these are the most desirable conditions under which to conduct commercial retorting. The crushing of the shale, besides costing something, would introduce dust troubles , and hand in hand with maximum oil production goes a very unsaturated oil. If liquid phase cracking was outstandingly successful on this oil, then a maximum production of oil might be a proper objective. The indications are that liquid phase cracking of the oil would be troublesome and wasteful. A limited amount of vapour phase cracking in the retort, or better still outside the retort under controlled conditions, produces an oil much higher in the lower boiling distillates, which are more valuable, and, while reducing yield to some extent, cuts down refining costs quite considerably. The writer leans more to the opinion as time goes on that a moderate amount of vapour phase cracking is desirable. On the other hand, the employment of excess steam has the opposite effect and, while desirable from an ammonia and gas producing point of view, in the Pumpherston retort, seems rather undesirable in the case of Tasmanite retorting, as the ammonia yield is commercially unimportant. In view of these considerations, especially the uncommercial ammonia yield, the employment of the Pumpherston retort - which was largely designed for ammonia recovery - has no definite advantage, except that it is a much more standardised retort than any other and its cost, operation, and capacity are well known from the experience in Scotland. It will admittedly retort the shale successfully, though it has not been tried for such a long period of time as the Crozier retort nor on as many grades of shale. For any future installation it would need serious consideration, though the bottom brick section is to some extent wasted on Tasmanite. It could be operated with much less steam that was usual in the Scotch practice.

The Crozier retort in its present form has successfully retorted thousands of tons of shale and, provided freak throughputs were not attempted, has proved very satisfactory in operation. It will produce 85% of the assay value of the shale, using little steam, and probably 90% or over if excess steam was used. There are no corresponding figures available on the Pumpherston retort working on Tasmanite and it is doubtful whether it would show any better recovery. The general nature of Tasmanite and the fact that the upper limit of its distillation range is 470°C. to 480°C. makes possible the use of a metal retort,

provided the dimensions are right and over driving is avoided.

The Crozier retort at present erected at Latrobe can be looked on as a 12 ton retort when operating on shale of 30-35 gallons assay value. It will produce under these conditions 350 gallons of oil per day. Richer or poorer shale is treated at a lower and higher throughput respectively, tending to keep the total oil production figure from serious variations. The diminution of the width of the retort would decrease the tonnage held in the retort but, by speeding up the shale current or travel, would result in a slight increase in oil production per retort.

In general there is not a great deal to chose between the Pumpherston and the Crozier retort. The latter has certainly had a more scientific and long continued tryout at Latrobe, so that commercial results on it are known. On the other hand, results on the Pumpherston can be fairly well predicted and there is no outstanding advantage one possesses over the other. Decision between the two would have to be made on the points of first cost, maintenance, and cost of operation.

Refining.

The question of refining Tasmanite shale oil distillates is intimately bound up with the nature of the product. Since lighting kerosene and lubricating oils are commercially out of question, the distillates between the boiling ranges of power kerosene and tractor fuel and bitumen residue must be disposed of as fuel oil or diesel oil.

This consideration reduces the refining problem to handling petrol, power kerosenes, and tractor fuel which is a heavier product than the power kerosene.

If a cheap reagent were available which would selectively act on the thiophenic sulphur and remove it without taking out serious quantities of unsaturateds and aromatics, the problem would be much simpler. None of the ordinarily used refining agents appear to do this. The Edeleanu process of extraction with liquid sulphur dioxide at low temperatures has not been tried, but so much of the oil would be soluble in the sulphur dioxide as to simply divide the oil into two fractions, of which the larger one contained most of the sulphur. The hypochlorite process is likewise inapplicable. Refining by the usual sulphuric acid method after a soda wash seems the cheapest and at a fairly high cost for acid and with high oil losses gives petrol of reasonable odour and colour, gum stable, non-corrosive, and passing the doctor test. The bulk of the thiophenic sulphur is, however, untouched.

After removal of creosote and hydrogen sulphide, the distillates contain appreciable quantities of basic oils, increasing in amount with the boiling point. The sulphuric acid used has to first dissolve these before it can remove gum-forming hydrocarbons like diolefines or remove sulphur compounds.

As regards the petrol fraction, 2% of sulphuric acid by volume is needed to produce a white spirit on subsequent distillation, though this spirit will then contain over 2% of sulphur and possess the characteristic odour. Increase of the acid to 4% results in a much better smell and somewhat decreased sulphur content, while 3% of oleum will do the same work and show a decreased sulphur content. It is thus possible, with relatively heavy reagent cost, to produce a petrol of standard/in all respects but sulphur content. quality

As regards power kerosene, and more so with heavier distillates, the position is not so good, as no commercially possible quantity of acid will remove the colour and characteristic smell, and the sulphur content is higher than with the petrol. It is necessary, therefore, to be content with an oil of high sulphur content possessing good combustion characteristics, but of decidedly yellor colour and relatively strong smell. The heavier grades of power kerosene are stronger coloured and of strong odour.

These distillates suit engines of high compression and run well even in compression ignition engines. The crude oil contains too much bitumen and unsaturated hydrocarbons to run well in at least some diesel engines though trial has been made, so that distillates in the kerosene range are more suitable. Fluid residuum that has been topped to 275°C. is unsuitable also, as it will not burn satisfactorily in the engine. Both crude oil and especially residuum give very heavy carbon deposits and it is this factor which prevents their use in diesel engines and not the combustion characteristics.

The distillates sold for diesel oils need practically no refining, as the corrosive sulphur compounds have been already distilled off from the oil.

Moderate vapour phase cracking of the oil vapours before condensation assists refining, as the more unsaturated hydrocarbons are thermally decomposed into carbon and hydrocarbons of greater value. Refining losses are thus diminished and lesser quantities of reagents are needed.

Liquid phase cracking has never been investigated, but it is anticipated that carbon deposition would be serious and yields are very problematical. High pressure hydrogenation would undoubtedly up-grade the oil but plant of this type is out of the question on a relatively small deposit as exists in the Latrobe area and if hydrogenation is commercially possible and economic, then the eastern Australian coalfields are the logical site.

In general, refining of Tasmanite shale oil distillates to usable products is possible at expenditures which are near to profitable working. These products are, however, not standard products to which the Australian public is accustomed and the extra treatment necessary to produce standard quality products in certain cases where this is possible seems decidedly uneconomic. For emergency use these high sulphur fuels would do very well and so the work that has been done is not in this sense wasted, though it may not lead to the establishment of the industry in the way it was formerly hoped.

Products and their Utilisation.

As foreshadowed in the previous section, refining problems are intimately bound up with the number of products made. If cracking were carried out, the number of products made could be reduced to two, petrol and fuel oil. Without resorting to cracking it is necessary to make the following products in order to dispose of the output and realise the highest value for the oil -

1. Petrol
2. Power Kerosene
3. Diesel Oil
4. Fuel Oil
5. Bitumen.

There is no very definite line of demarcation existing between 2 and 3, and between 3 and 4. During part of this year (1933) the whole output has been sold as fuel oil, but the above division enables a higher net return to be secured, provided the output is sufficient for economic refining.

Lubricating oils, waxes, and lighting kerosene have to be excluded from the possible range of products and it will be noticed that, with the exception of the bitumen, all the others fall in the fuel category. The small amounts of creosote etc. available are not considered to be important, but may produce some revenue.

The last three products, diesel oil, fuel oil, and bitumen, with proper works control may be turned out to standard specifications, but petrol and power kerosene are subject to the limitations discussed in the previous section. As regards these two latter products, lorries and other vehicles have done many thousands of miles on these high sulphur fuels without apparent damage to the engine. Crank case and exhaust pipe corrosion would seem to be the most obvious troubles to be met with though the continued exposure of valves etc. to gases containing appreciable amounts of sulphur dioxide may be equally serious.

Work is required on high sulphur fuels to give information on these points and the Tasmanite shale oil petrol provides a very suitable high sulphur fuel, since it is non-corrosive in fuel lines etc. If corrosion is merely confined to crankcases and exhaust pipe, the substitution of stainless steel would overcome this difficulty and the disadvantage of the high sulphur fuel would then be mainly that of obnoxious exhaust gases.

The shale bitumen has usually been considered as a good product, but the quantity is only 1.5% of the weight of shale retorted. Treatment on the lines indicated in Part II of this monograph, i.e., heating the shale to 400°C. in the presence of the oil vapours produced, will convert most of the kerogen into bitumen. Subsequent extraction

of this bitumen by solvents will give a 20% yield of bitumen of a consistency suitable for road making in the case of the richer shales. This process has not reached any commercial prominence, though a patent exists covering some of the ground. As a possible method of utilisation of the shale, instead of oil production, it is hard to say without further work whether it would be profitable in the event of a sufficiently large market being available.

Future of the Industry.

Attempts to work the Latrobe Shale have extended over two decades and, while the work that has been done during the past six years on the field is the most valuable of all, the establishment of the industry on a profitable basis seems nearly as far off as ever.

The reasons for this state of affairs may be summed up in a few words in two main statements

1. The grade of the shale is on the average too low to allow of economic working.

2. The nature of the oil produced is such that refining costs and losses are high and standard quality products cannot be made on an economic basis.

These are the main and controlling issues which determine the fate of an industry which has most other things in its favour. Markets exist at the door, wood, coal, and water are readily available, sea and rail transport are close at hand, the shale seam is of workable thickness and only gently inclined, the climate is very good, labour is available, and last but not least capital has been freely subscribed in the past. Despite all these advantages, what is tantamount to failure has marred the attempts to put the industry on a working basis, simply because of the two main issues noted above. Had five percent of the money that has been spent on plant etc. been applied to a proper investigation of the shale and its distillation products and to an oil survey of the known shale occurrences, much of the remaining capital could have been saved and the sum total of the knowledge of the shale would be much greater than it is today. Once again the importance of laboratory and small scale research work has been demonstrated and it cannot be too strongly emphasised that any sound development of industry must have for its basis properly planned and conducted research work.

PART IX.

COMPARATIVE WORK ON NEW SOUTH WALES OIL SHALES.

These shales are of a different type and are much freer from mineral matter. The richest Tasmanite shales exceed 60% ash, so that the comparative richness of the New South Wales shales is indicated by the proximate analyses given below. The New South Wales shales in the air dried condition contain 0.3 to 0.4% moisture, but for the purposes of comparison they are given on the moisture free basis.

	Rich Tasmanite Shale.	Hartley Vale.	Newmes	Capertee No. 1.	Capertee No. 2.
Volatiles at 900°C.	31.75%	75.55%	50.9 %	61.15%	55.9 %
Fixed Carbon	1.75	7.0	13.2	14.60	18.0
Ash	66.50	17.45	35.9	24.25	26.1
Sulphur	2.60	0.40	0.41	0.52	0.58

It will be seen that typical New South Wales shales from different areas are all much richer than rich top seam Tasmanite shale. The production of fixed carbon is relatively greater with the New South Wales shale. The sulphur content of the Tasmanite shale much exceeds that of the New South Wales shales and the intrinsic sulphur content of the kerogen of the Tasmanite is approximately 3.7%, whereas the corresponding figure for the New South Wales shales, although not determined, must be approximately of the order of one tenth of the figure quoted for Tasmanite, since there is some pyritic sulphur in the New South Wales shale, especially in the Capertee samples.

The production of oil much lower in sulphur is therefore to be expected from New South Wales shale and this is in accord with the fact that New South Wales shale oil distilled under laboratory conditions contains about one-eighth of the sulphur content of Tasmanite shale oil.

A number of distillations have been made on different samples of New South Wales shales and for comparative purposes it is sufficient to select the following runs.

Run 101	Distillation of	Hartley Vale Shale.	
102	"	"	Newmes shale.
103	"	"	Capertee Valley shale, Sample No. 1.
104	"	"	Capertee Valley shale, Sample No. 1, with vapour phase cracking.
105	"	"	Capertee Valley shale, Sample No. 2.

The distillations were carried out in the same apparatus as described in Part III and the data obtained are reported in the following pages on a similar plan to that already used. The only additional data are the calorific values of the scrubbed gas from the Newnes and Capertee No. 2 samples.

The rates of temperature rise of the retort wall and the centre of the charge together with the progressive total oil yield and progressive gas flow are shown in graphical form in the attached prints for Runs 101, 102, 103 and 105.

RUN No. 101.

Charge 896 grams of dried shale from Hartley Vale, N.S.W., in pieces not exceeding 1" size.
Room temperature 16°C. Barometer 765 m.m.
Gas scrubbed from hydrogen sulphide and metered.
Ammonia recovery completed by dilute sulphuric acid scrubbing.
Oil scrubber catches in order 5 m.l. and 5 m.l. = 2.5 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON	GAS FLOW LITRES/HOUR.
2.45	210	138		
3.00	258	173		
3.15	293	210		
3.30	330	258		
3.45	363	301		
4.00	386	334		
4.15	412	363	1.0	1.0
4.20				3.0
4.25				4.2
4.30	434	388	2.5	5.0
4.35				7.2
4.40				10.0
4.45	457	410	13.2	15.0
4.50				20.3
4.55				25.4
5.00	468	433	42	31.4
5.05				34.5
5.10				38.3
5.15	479	440	90	41.7
5.20				43.5
5.25				41.2
5.30	497	469	144	36.3
5.35				31.0
5.40				26.3
5.45	514	498	160	21.8
5.50				15.0
5.55				12.5
6.00	527	513	164	11.4
6.05				10.8
6.10				9.5

Run No. 101 continued.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL PRODUCTION GALLONS/TON.	GAS FLOW LITRES/HOUR.
6.15	540	530	166.5	8.5
6.20				6.8
6.25				5.0
6.30	552	538	166.5	4.2
6.35				3.5

Water commenced to distil over at 3.10 p.m. and oil at 4.10 p.m.
Heating power cut off 6.30 p.m.

Water condensed gallons per ton	2.5
Oil Yield gallons per ton	166.5
Specific gravity of oil	0.870
Sulphur content of oil	0.29%

Distillation analysis of crude oil 100 m.l.

Up to 150°C.	11.1%
150°C.-,200°C.	7.2
200°C.- 250°C.	8.8
250°C.- 300°C.	12.8
300°C.- 350°C.	15.5
350°C.- 400°C.	19.1
Loss & residue	25.5

Residue

Weight 243 grams Percentage of shale 27.1

Proximate analysis of residue

Volatiles 4.0% Fixed Carbon 35.4% Ash 60.6% Sulphur 0.56%

Sulphur distribution in products of distillation

Residue	46.5%
Oil	38.0
Hydrogen sulphide	24.2
Other gases and loss (over recovery)	8.7

General Data

Ash/shale ratio	0.164
Kerogen percentage	83.6%
Distillation Index	1.99
Rate of heating in distillation range per hour	70°C.
Maximum rate of oil production	216 galls/ton/hour
do. per % kerogen	2.58 do.
Total time of oil production	2 hours.

Run No. 101 continued.

General Data continued.

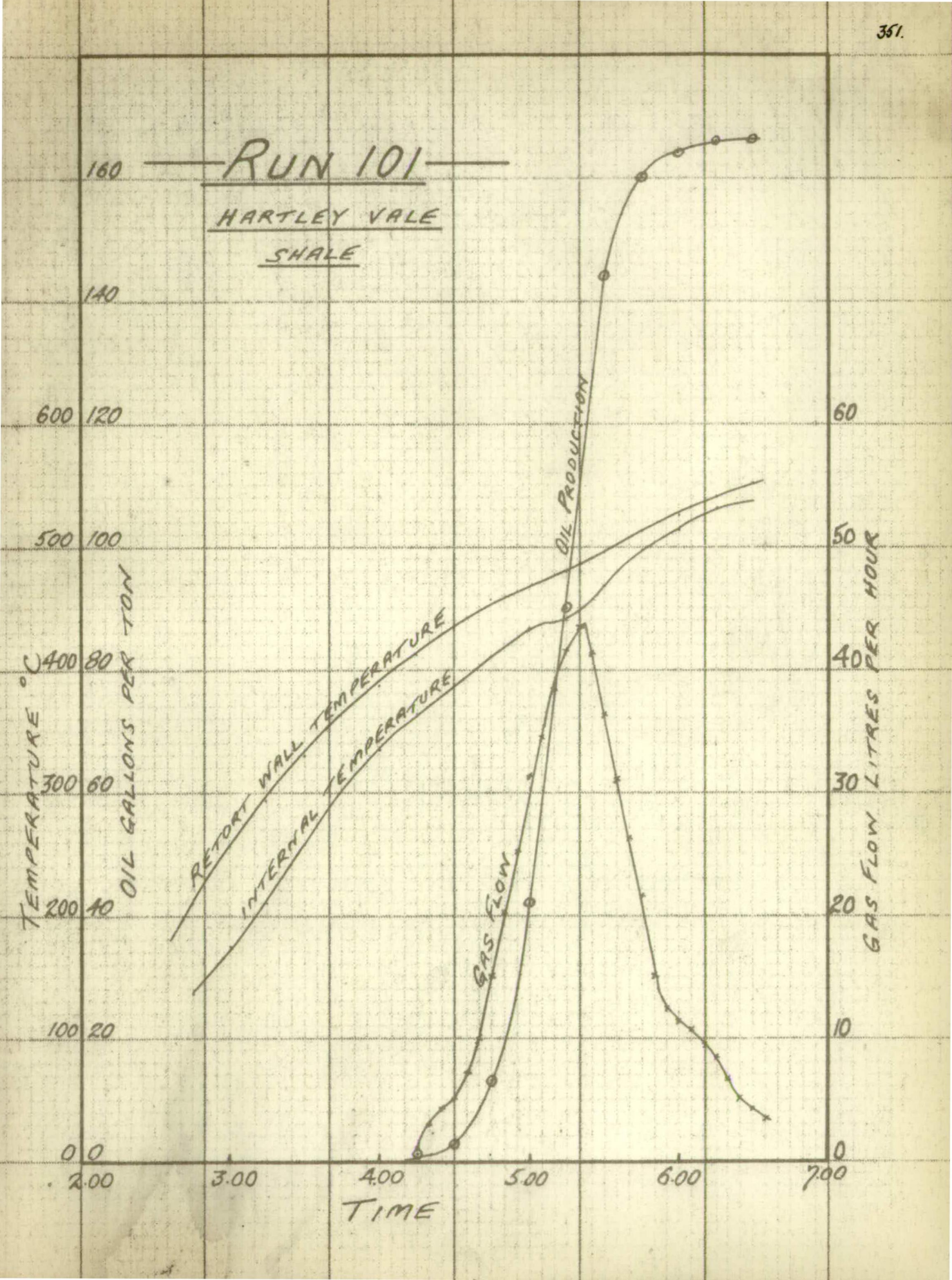
Ammonium sulphate yield lbs/ton		0.40	
Gas production	Carbon dioxide	not determined	
	Hydrogen sulphide	24	cu. ft. /ton N.T.P.
	Scrubbed gas	1670	do.
	Total gas	1694	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	16.4	-
Volatiles in residue	1.08	1.30
Fixed carbon in residue	9.60	11.50
Oil	64.50	77.15
Water condensed	1.12	1.35
Hydrogen sulphide	.10	.10
Other gases and loss	7.20	8.60
	100.00	100.00

RUN 101

HARTLEY VALE SHALE



RUN No. 102.

Charge 896 grams of dried shale from Newnes, N.S.W., broken to 1" size.
This sample was procured by the Newnes Investigation Committee.
Room temperature 12° C. Barometer 754 m.m.
Oil scrubber catches in order 5.5, 6.0, 3.0, and 1.5 m.l. = 4.0 gallons per ton.
Furnace switched on 9.04 a.m. Cut off for about 30 minutes to make adjustments. Switched off 3.30 p.m.
Gas scrubbed to remove hydrogen sulphide, metered, and burnt in a gas calorimeter.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL YIELD GALLONS/TON	GAS FLOW LITRES/HOUR.
11.15	271	216		
11.30	305	245		
11.45	331	272		
12.00	335	303		
12.15	379	332		
12.30	404	357		1.4
12.35				2.1
12.40				2.1
12.45	425	379	0.2	3.1
12.50				4.2
12.55				4.2
1.00	440	401	0.8	5.0
1.05				6.5
1.10				7.5
1.15	460	416	9.5	9.7
1.20			15.0	12.2
1.25				15.3
1.30	474	429	29.5	17.0
1.35				18.3
1.40				19.5
1.45	487	440	58.0	20.4
1.50				21.2
1.55				20.7
2.00	501	457	83.5	20.4
2.05				19.4
2.10				18.3
2.15	516	482	100.5	17.4
2.20				16.7
2.25				15.9
2.30	531	505	107.5	14.6
2.35				13.6
2.40				11.0
2.45	540	522	109.0	9.2
2.50				7.8
2.55				7.2
3.00	546	533	109.2	6.5
3.05				5.5
3.10				5.2
3.15	555	543	109.2	5.0
3.30	558	550	109.2	4.2

Run No. 102 continued.

Water condensed gallons per ton	2.2
Oil Yield	109.2
Specific gravity of crude oil	0.874
Sulphur content of crude oil	0.33%
Saturation of crude oil	36 %

Distillation analysis of crude oil	100 m.l. A.S.T.M.
Up to 150°C.	8.5 %
150°C.- 200°C.	8.0
200°C.- 250°C.	9.5
250°C.- 300°C.	11.5
Residuum at 300°C.	62.5
	100.0

Residue

Weight 469 grams Percentage of shale 52.3%

Proximate analysis of residue

Volatiles 4.75% Fixed carbon 25.65% Ash 69.6% Sulphur 0.34%

Sulphur distribution in products of distillation

Residue	43.2%
Oil	32.85
Hydrogen sulphide	23.35
Other gases etc.	0.6

General Data.

Ash/shale ratio		0.364	
Kerogen percentage		63.6	
Distillation Index		1.72	
Rate of heating in distillation range		65°C.	per hour
Maximum rate of oil production		114	galls/ton/hour
do. per % kerogen		1.79	do.
Total time of oil production		2	hours
Gas production	Carbon dioxide	59	cu. ft./ton N.T.P.
	Hydrogen Sulphide	23	do.
	Scrubbed gas	1265	do.
	Total gas	1347	do.

Average calorific value of scrubbed gas gross B.Th.U./cu.ft. N.T.P.	1295
Average calorific value of scrubbed gas nett do.	1220
Highest calorific value of scrubbed gas gross B.Th.U./cu.ft. N.T.P.	1435
Calorific value of gas at end of oil production gross do.	1255

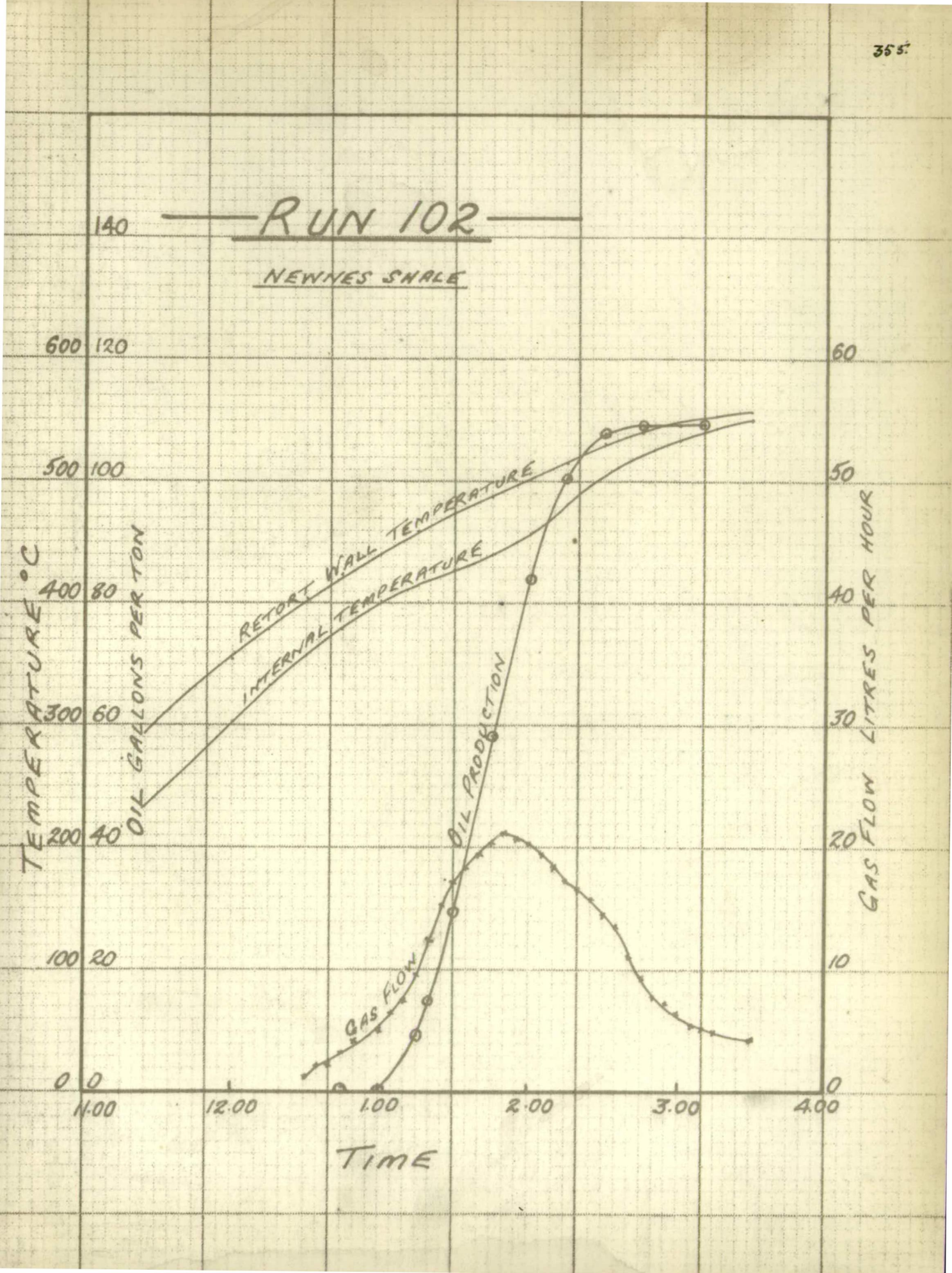
Run No. 102 continued.

Weight Balance on products of distillation.

	Percentage of shale	On ashless basis.
Ash	36.40%	
Volatiles in residue	2.50	3.95%
Fixed carbon in residue	13.40	21.05
Oil	43.25	68.00
Water condensed	1.00	1.60
Carbon dioxide	0.40	0.60
Hydrogen sulphide	0.10	0.15
Gas etc. by difference	2.95	4.65
	100.00	100.00

RUN 102

NEWNES SHALE



RUN No. 103.

Charge 896 grams of dried shale from the Capertee Valley, N.S.W. in pieces not exceeding 1" size.
Room temperature 17°C. Barometer 746 m.m.
Switched on 12.05 p.m., off 5.15 p.m.
Gas scrubbed from hydrogen sulphide and metered.
Ammonia recovery completed by dilute sulphuric acid scrubbing.
Oil scrubber catches in order 3 m.l. and 4 m.l. = 1.75 gallons per ton.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL YIELD GALLONS/TON	GAS FLOW LITRES/HOUR.
2.00	351	297		
2.15	384	338		
2.30	409	367		
2.40				2.0
2.45	433	396	1	6.0
2.50				7.3
2.55				8.5
3.00	455	417	10	12.3
3.05				15.0
3.10				20.3
3.15	470	433	31	26.1
3.20				30.2
3.25				32.5
3.30	487	451	69	33.7
3.35				33.7
3.40				33.7
3.45	503	478	99	32.0
3.50				30.2
3.55			~~116~~	28.1
4.00	524	504	116	26.1
4.05				25.1
4.10				23.0
4.15	538	527	123	21.7
4.20				20.0
4.25				18.0
4.30	553	541	128	17.0
4.35				15.4
4.40				13.5
4.45	568	536	129	12.5
4.50				10.8
4.55				9.5
5.00	580	574	130	8.4
5.15	592	586	130	6.8

Oil commenced to distil over at 2.37 p.m.

Run No. 103 continued.

Water condensed gallons per ton	2.0
Oil yield gallons per ton	130.0
Specific gravity of oil	0.873
Sulphur content of oil	0.32 %

Distillation analysis of crude oil	100 m.l.
Up to 150°C.	12.0%
150°C.- 200°C.	8.7
200°C.- 250°C.	10.3
250°C.- 300°C.	12.5
300°C.- 350°C.	16.0
350°C.- 400°C.	20.0
Residue + loss	20.5
	100.0

Residue

Weight 381 grams. Percentage of shale 42.5%

Proximate analysis of residue

Volatiles 4.5% Fixed carbon 40.45% Ash 55.05% Sulphur 0.44%

Sulphur distribution in products of distillation

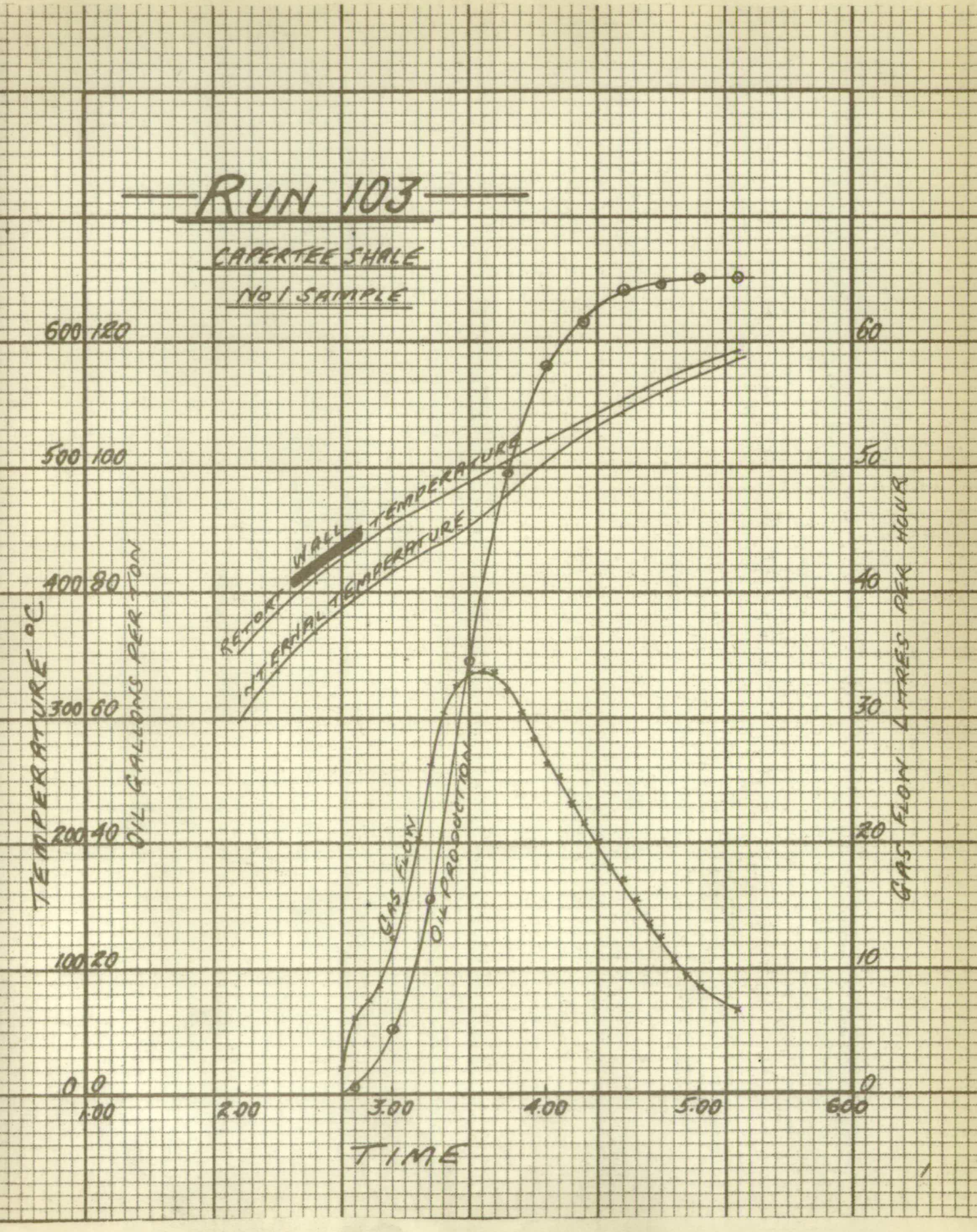
Residue	31.8%
Oil	27.0
Hydrogen sulphide	18.0
Other gases and unaccounted for	23.2

General Data

Ash/shale ratio		0.234	
Kerogen percentage		76.6%	
Distillation Index		1.70	
Rate of heating in distillation range		75	deg.C/hour
Maximum rate of oil production		152	galls/ton/hour
do. per % kerogen		1.98	do.
Total time of oil production		2	hours
Ammonium sulphate yield lbs/ton		1.04	
Gas production	Carbon dioxide	not determined	
	Hydrogen sulphide	28	cu.ft./ton N.T.P.
	Scrubbed gas	1840	do.

Weight Balance on products of distillation

	Percentage of shale	On ashless basis
Ash	23.40%	
Volatiles in residue	1.91	2.50%
Fixed carbon in residue	17.19	22.40
Oil	50.45	65.90
Water condensed	0.90	1.20
Hydrogen sulphide	0.11	0.15
Other gases and loss	6.04	7.85
	100.00	100.00


RUN 103
CAPERTEE SHALE
No 1 SAMPLE
600 120
500 100
400 80
300 60
200 40
100 20
0 0
TEMPERATURE °C
OIL GALLONS PER TON
WALL TEMPERATURE
REACTOR
MATERIAL TEMPERATURE
GAS FLOW
OIL PRODUCTION
60
50
40
30
20
10
0
GAS FLOW M³ PER HOUR
1.00
2.00
3.00
4.00
5.00
6.00
TIME

RUN No. 104.

Charge 896 grams of Capertee shale as used in Run No. 103.
Room temperature 18°C. Barometer 760 m.m.
Heating power switched on 11.50 a.m. Current cut down 3.20 p.m. to check temperature rise, increased current at 3.35 p.m. and again at 3.45 p.m. to full heating current.
Gas scrubbed to remove hydrogen sulphide and metered.
Oil scrubber catches parallel to Runs 33 and 103 in order 7 and 5 m.l. = 3 gallons per ton.
A further oil scrubber containing 250 m.l. of kerosene absorbed another 3 gallons per ton of spirit which is not shown in the oil yield figures in the tabulation to keep the comparison correct with Runs 33 and 103.
The oil vapours before condensing were passed through the cracking tube as in Run 33 packed with granular Capertee retort residue from Run 103. Weight used 120 grams.

TIME P.M.	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE	OIL YIELD GALLS/TON	GAS FLOW LITRES/HR.	CRACKING TUBE TEMPERATURE.
2.50	443	398	1.0	6.0	441
3.00	456	414	8.0	13.0	520
3.15	468	422	26.0	33.0	555
3.25				32.0	
3.30	467	437	39.0	30.3	552
3.35				27.5	
3.40				24.8	
3.45	456	441	71.0	22.5	552
3.50				22.0	
3.55				23.0	
4.00	467	447	81.0	24.0	567
4.10				27.5	
4.15	484	465	90.0	25.5	566
4.20				26.0	
4.25				26.0	
4.30	502	482	99.0	26.5	566
4.35				26.5	
4.40				25.5	
4.45	519	505	107.0	25.0	572
4.50				24.5	
4.55				23.6	
5.00	534	522	112.0	22.8	579
5.05				21.8	
5.10				20.6	
5.15	548	538	115	20.0	585
5.30	562	555	117	16.0	587
5.45	574	570	118	11.0	587

Water condensed gallons per ton 1.75
Oil yield without additional scrubber 118 gallons per ton
Oil yield with do. 121 do.
Specific gravity of oil 0.864
Sulphur content of oil 0.48%

Run No. 104 continued.

Partial Distillation analysis of crude oil	400 m.l.
Up to 150°C.	13.0%
150°C.- 175°C.	6.4%
175°C.- 300°C.	33.0%
Residuum + loss	47.6%

Residue

Weight	387 grams	Percentage of shale	43.2%

Gain in residue in cracking tube 9 grams.

Gas volume - scrubbed gas 2490 cu.ft./ton N.T.P.

A similar vapour phase cracking run was made with the cracking tube at a higher temperature averaging about 650°C. An additional oil scrubber was used compared with Run 104.

The condensed oil was 66 gallons per ton of 0.63% sulphur and of higher density than usual 0.906 while the scrubber catch was 14 gallons per ton making a total of 80 gallons per ton. The crude condensed oil was largely aromatic in nature and comparatively volatile for its high specific gravity.

200 m.l. on distillation gave 26.5% below 175°C. with an additional 22% 175-300°C. No further work was done on this run so that it has not been given a serial number.

RUN No. 105.

Charge 896 grams of dried shale from Capertee Valley broken to 1" size.
This sample was procured by the Newnes Investigation Committee.
Room temperature 8°C. Barometer 758 m.m.
Oil scrubber catches in order 5, 6.5, 4.5, 3.0 m.l. = 4.75 gallons per ton.
Furnace switched on 9.05 A.M., off 2.45 P.M.
Gas scrubbed to remove hydrogen sulphide, metered, and burnt in a gas calorimeter.

TIME	RETORT WALL TEMPERATURE	RETORT CENTRE TEMPERATURE.	OIL YIELD GALLONS/TON	GAS FLOW LITRES/HOUR.
10.05	178	71		
10.33	255	152		
10.47	284	187		
11.05	317	235		
11.15	337	262		
11.30	358	298		
11.45	382	329		
12.00	403	355		
12.15	423	378		2.8
12.20				2.8
12.25			0.5	3.8
12.30	437	396	1.2	4.2
12.35			2.8	4.9
12.40			4.2	6.0
12.45	452	413	7.5	7.0
12.50			12.2	9.5
12.55				11.7
1.00	468	426	24.0	14.2
1.05				15.7
1.10				18.7
1.15	478	438	52.0	20.3
1.20				21.8
1.25				22.7
1.30	492	452	85.0	23.5
1.35				-
1.40				23.8
1.45	507	475	108.0	23.5
1.50				22.7
1.55				22.1
2.00	521	498	121.0	20.3
2.05				18.3
2.10				16.3
2.15	535	521	124.0	14.2
2.20				12.0
2.25				11.0
2.30	547	536	124.5	10.0
2.35				9.5
2.40				9.0
2.45	558	550	124.25	8.5
2.50				
2.55	556	556		
3.00	539	546	124.25	

Run No. 105 continued.

Water condensed gallons per ton	2.8
Oil yield gallons per ton	124.25
Specific gravity of oil	0.865
Sulphur content of oil	0.36%
Saturation of oil	36%

Distillation analysis of crude oil — 100 m.l. A.S.T.M.

Up to 150°C.	9.0%
150°C.- 200°C.	8.1
200°C.- 250°C.	9.9
250°C.- 300°C.	12.0
Residuum etc.	61.0
	100.0

Residue

Weight 415.5 grams Percentage of shale 46.4%

Proximate analysis of residue

Volatiles 6.2% Fixed Carbon 40.15% Ash 63.65% Sulphur 0.60%.

Sulphur distribution in products of distillation

Residue	47.9%
Oil	28.55
Hydrogen sulphide	23.0
Other gases and loss	0.55

General Data

Ash/shale ratio		.2495	
Kerogen percentage		75.05	
Distillation Index		1.66	
Rate of heating in distillation range		65°C.	per hour
Maximum rate of oil production		132	gallons/ton/hour
do. per % kerogen		1.76	do.
Total time of oil production		2	hours
Gas production	Carbon dioxide	66	cu.ft./ton N.T.P.
	Hydrogen sulphide	31	do.
	Scrubbed gas	1350	do.
	Total gas	1447	do.

Average calorific value of scrubbed gas	gross	B.Th.U./cu.ft. N.T.P. 1330
" " " " " "	nett	do. 1265
Highest " " " " " "	gross	do. 1430
Calorific value at end of oil production	gross	do. 1255

Run No. 105 continued.

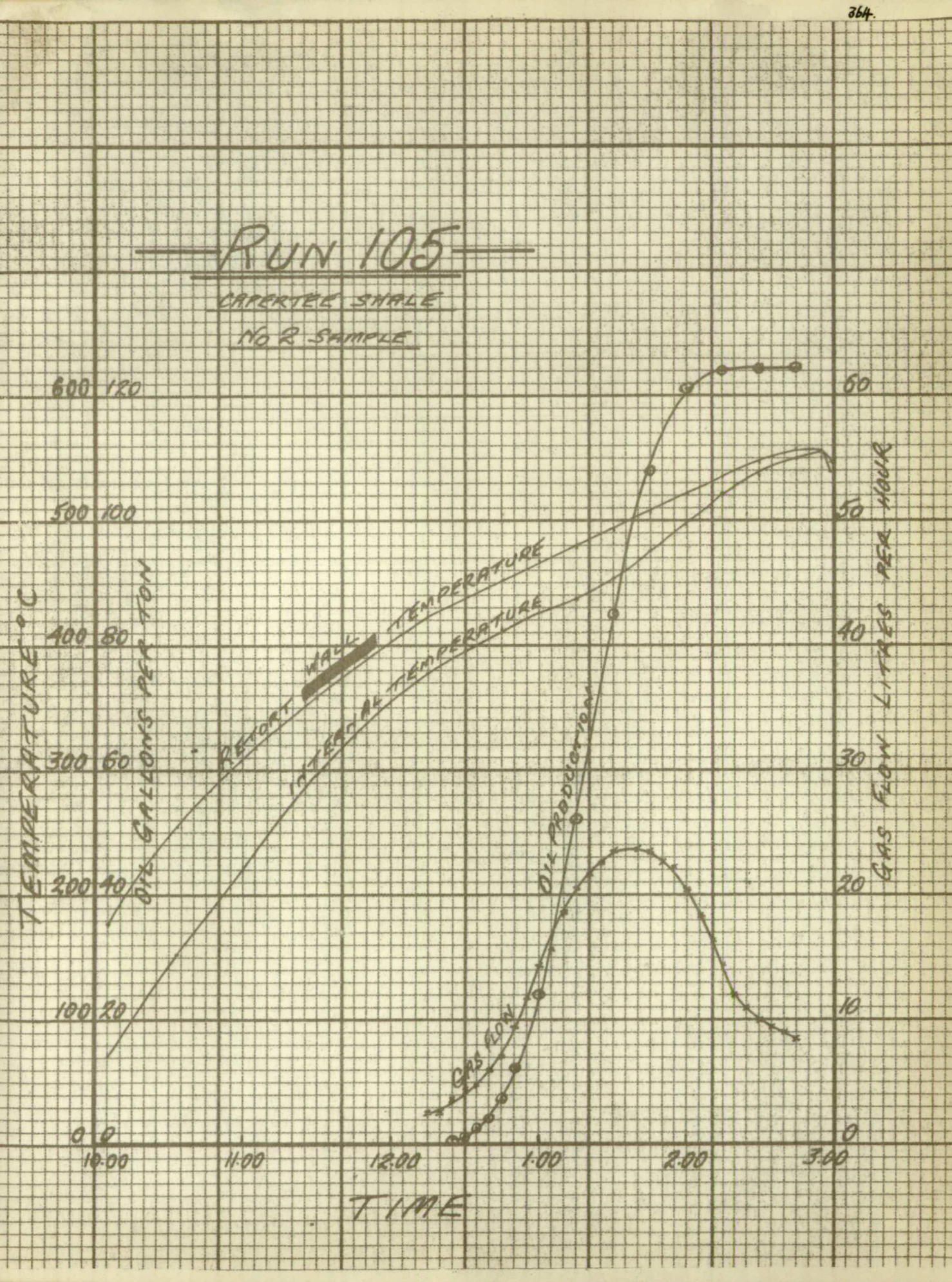
Weight Balance on products of distillation

	Percentage of shale.	On ashless basis.
Ash	24.95	
Volatiles in residue	2.90	3.85
Fixed carbon in residue	18.65	24.85
Oil	48.95	65.25
Water	1.25	1.65
Carbon dioxide	0.45	0.60
Hydrogen sulphide	0.13	0.17
Gas etc. by difference	2.72	3.63
	100.00	100.00

RUN 105

CARBERRY SHALE

NO 2 SAMPLE



DISCUSSION OF RETORTING RESULTS.

The nature and composition of the New South Wales shale kerogen being different from that of Tasmanite it is not surprising that some differences are to be noted in the retorting of the two types of shale. The more outstanding points are covered under the following headings.

Caking of shale in retorting.

The Tasmanite shale is too poor or, in other words, the kerogen is too much diluted with mineral matter to cake strongly even in the case of the richest samples, but with the New South Wales shales the smaller amount of ash coupled with a stronger caking tendency causes the formation of a coke-like retort residue. In the case of the Hartley Vale shale the charge apparently fused completely and left a residue of dense hard coke which took hours to chip out of the retort. The other shales were higher in ash and the organic matter also appeared to be somewhat different so that the retort residue retained substantially the form of the original shale particles. The commercial retorting of shale similar to the rich Hartley Vale sample would be very difficult indeed if the sample used was a representative one.

Temperature range of oil production.

The different nature of the organic matters of the Tasmanian and New South Wales shales was indicated by higher temperatures being necessary in the latter case for both the preliminary expulsion of water and for the oil production proper. The expulsion of water from the kerogen is the first indication of serious decomposition, and this begins at 230°C.-240°C. in the case of Tasmanite kerogen, while the New South Wales kerogen requires a temperature of 270°C.-280°C. The production of oil in the case of Tasmanite begins at 350°C. and at 400°C. is progressing at a steady rate and is complete at 470°-480°C. depending somewhat on the previous heat treatment of the shale. With New South Wales shales no oil distillate is produced until the retort wall temperature reaches approximately 420°C. Excepting the Hartley Vale sample, less than one gallon per ton has distilled off with a retort wall temperature of 440°C. while 90% of the oil is over when the centre of the charge reaches 480°C. The greater part of the oil production takes place between the temperatures of 430°C. and 480°C. It is necessary to exceed 500°C., say run up to 520°C., to recover the remaining oil, though 99% of the total yield is obtained by an upper temperature of 505°C. Above 520°C. only gas is produced, together with increasing quantities of ammonia. In Run 103 it would appear that a temperature in excess of 520°C. is necessary for the recovery of the last traces of oil, but in this run one end of the retort was somewhat cool, accounting for this difference. The last oil to come over is very red in colour.

Gas yield in relation to kerogen.

In general the New South Wales shales produce less gases of all kinds per unit of kerogen than the richest Tasmanite shales. The former produce

on the average much less water, somewhat less carbon dioxide, and very much less hydrogen sulphide than the latter. As regards scrubbed gas, the former produce under laboratory conditions about 20 cu. ft. at N.T.P. per unit of kerogen, while the latter produce approximately 30 cu. ft. Tasmanian retort gases are usually in the vicinity of 25% hydrogen sulphide and in some cases 30% is reached, while the highest percentage in the New South Wales shales examined was 2% in the case of Capertee shale, the others being less. Considered in relation to the kerogen and so indirectly to the oil yield, the amount of hydrogen sulphide produced in retorting the New South Wales shales is only several per cent. of the corresponding figure for Tasmanite.

Efficiency of conversion of kerogen to oil.

The amount of kerogen converted into oil in the case of the New South Wales shales examined ranges from 62.25% to 77.15%. The latter high figure is for the rich Hartley Vale shale, while the Newnes and Capertee representative samples gave figures of 68.0% and 65.25%. These figures are fairly close to the conversion efficiencies for the highest grade Tasmanite shales distilled under the same conditions. The distillation index which does not take into account the specific gravity of the oil is relatively somewhat lower for the Tasmanite as these oils average around 0.92 specific gravity as against 0.87 for the New South Wales oils. The efficiency of conversion of kerogen into oil showed a distinct increase in the case of the rich Hartley Vale sample, but a sufficient range of samples was not examined to establish any such relation as exists between the richness and conversion efficiency in the case of Tasmanite shale.

Vapour phase cracking of the oil vapours issuing from the retort.

A little work was carried out on these lines as reported under Run 104 on the Capertee No. 1 sample. This run was made under conditions very similar to those of Run 33 on the standard sample of Tasmanite shale. A cracking tube temperature of approximately 560°C. was chosen as at this temperature no oil nor pitchlike compounds condense in the cracking tube and cracking is not so destructive as to change the general nature of the oil as happens at high temperatures. At the same time a useful amount of cracking does occur and reaction is sufficiently rapid to utilise the cracking commercially. The comparative behaviour of Capertee and Tasmanite shale oils under vapour phase cracking can be seen approximately from the following data, where Runs 33 and 104 are contrasted along with parallel runs on the same samples with vapour phase cracking omitted.

	Tasmanite Shale.		Capertee Shales.	
	Run 23, Simple distillation.	Run 33, Vapour phase cracking.	Run 103, Simple distillation.	Run 104, Vapour phase cracking.
Charge	1120 grams	1120 grams	896 grams	896 grams.
Oil grams	241	152.5	453	406
galls/ton	52.3	34.2	130	118
Time of oil production	$1\frac{1}{4}$ hrs.	2 hrs.	2 hours	3 hours
Gas yield scrubbed cu.ft/ton	1018	1481	1840	2490
total	1275	1765	1936	2600 approx.
total litres	39.8	55.1	48.4	65
Approx. Vol. oil vapours ass. mol. wt. 224	24.1	15.2	45.3	40.6

Run 15 would have been better to take than Run 23 in some respects, but the gas figures were not determined. However, in Run 15, 244 grams of oil was produced so that the difference is not great.

If the figures for oil volume and gas volume for Runs 23 and 103 be accepted as the volumes entering the cracking tube, we have

	Volume entering tube.	Volume leaving tube.
Tasmanite shale	64 litres N.T.P.	70 litres N.T.P.
Capertee shale	94 do.	106 do.

The volumes are approximately for the two shales in the ratio of 2:3, which is also the ratio of the oil production or cracking times, so that the vapour + gas would have approximately the same heat effect per unit volume of gas. The Capertee mixture of gases and oil vapours issuing from the retort was decidedly richer in oil vapours so that a greater decomposition of the Capertee oil would reasonably be expected. The reverse is true, however, and 47 grams of the Capertee oil is decomposed as against 88 grams of the Tasmanite oil. It would appear that Tasmanite oil owing to its highly unsaturated nature is about twice as easily decomposed in vapour phase cracking. The comparison is obscured by the fact that the back pressure due to the cracking tube appeared to cause more fixed carbon and volatile matter to be left in the retort residue in Run 33 which was larger in amount than usual. It does not alter the conclusions drawn as the ratio of the gains in the cracking tube residue in Runs 33 and 104, which is an approximate index of the oil decomposition, is 19:9 or, say, 2:1, thus confirming the conclusion drawn above. As regards the actual time of contact in the hot cracking zone, assuming 35 litres at N.T.P. per hour as the average flow and the free space in the 300 c.cm. hot zone as 80% of the total, which is near the actual figure, the time of contact at 560°C. is 8 seconds. If the intra particle porosity was not available as reaction space, then the contact time comes down to approximately 5 seconds.

The cost of vapour phase cracking would not be very great on the large scale, so that the method has some promise as a cheap means of producing a greater proportion of straight run petrol compared with ordinary distillation. In addition, vapour phase cracking undoubtedly decomposes the highly unsaturated compounds which are most easily attacked by sulphuric acid and so decreases refining costs. In laboratory experiments the petrol distilled from the vapour phase cracked oil took decidedly less acid to refine it gum stable. The colour of the redistilled refined petrol from the cracked oil was very good - far superior to commercial petrol.

As in the case of Tasmanite oil, vapour phase cracking increases the sulphur content of the crude oil.

NEW SOUTH WALES SHALE OILS.

In addition to the oils obtained in the laboratory distillations of Hartley Vale, Newnes, and Capertee shales, three other samples of New South Wales shale oil have been examined. These were Capertee and Newnes oils distilled in the 100 lb. retort in the low temperature distillation laboratory, Mines Department, Melbourne, and a sample of the oil produced at Newnes during the run under the supervision of the Shale Oil Development Committee Ltd. The latter oil was deficient in the lower boiling oils - containing very little petrol so that it can hardly be compared with the other oils as regards volatility, but the work on the fractions from this oil as regards composition is valuable in indicating the differences to be expected in a commercial oil compared with a laboratory produced oil.

The work carried out is conveniently reported in the following order:-

1. Distillation analyses of the various oils.
2. Specific gravity, saturation and sulphur content of crude oils and distillates.
3. Composition of New South Wales shale oil distillates.
4. Refining of New South Wales Shale Oil distillates.

DISTILLATION ANALYSES OF THE VARIOUS OILS.

The following distillation analyses performed in the standard A.S.T.M. apparatus indicate the volatility of the crude oils distilled under varying conditions.

No. 1 oil distilled from Capertee shale in 2 lb. retort.
No. 2 " " " " " " 100 lb. retort.
No. 3 " " " Newnes " " 2 lb. retort.
No. 4 " " " " " " 100 lb. "
No. 5 " " " " " " Commercial retorts.

In the cases of oils 1-4 the condensation has been fairly complete but the scrubber spirit has not been added to the oil.

100 m.l. distillation analyses.

Oil No.	1	2	3	4	5
Initial B.Pt.	76°C.	76°C.	82°C.	89°C.	148°C.
10% over	159	156	163	158	212
20% "	216	211	220	206	261
30% "	265	256	270	251	297
40% "	304	295	310	288	326
50% "	334	322	338	320	338

Oils 2, 4, and 5 were also distilled in 800 m.l. batches in a litre flask without a rectifying column with the following results:-

800 m.l. distillation analysés.

Oil No.	2	4	5
Initial B.Pt.	69°C.	70°C.	120°C.
10% over	171	170	228
20% "	220	218	267
30% "	263	257	299
40% "	299	292	332
50% "	332	323	352

From the volatility curves drawn from the 100 m.l. distillation results the following amounts of fractions - 170°C., 170°C.- 230°C., and 230°C.- 300°C. were read off.

Percentage of Fractions 100 m.l. distillations.

Oil No.	1	2	3	4	5
Fraction - 170°C.	12.0%	13.0%	11.4%	13.0%	3.2%
170°C.- 230°C.	11.0%	11.0%	10.6%	12.5%	10.6%
230°C.- 300°C.	16.0%	18.0%	15.5%	18.1%	17.4%

Oils 2, 4, and 5 were distilled in a litre flask using 800 c.c. charges and the receivers were changed at 170°C., 230°C. 300°C., 350°C., and in one case 375°C. The following were the results obtained.

Percentage of fractions 800 m.l. distillations.

Oil No.	2	4	5
Fraction - 170°C.	9.9%	10.1%	1.3%
170°C.- 230°C.	12.4%	13.0%	9.2%
230°C.- 300°C.	18.6%	20.2%	19.8%
300°C.- 350°C.	16.4%	19.0%	18.9%
350°C.- 375°C.	38.7%	12.3%	18.7%
375°C.- end		21.4%	25.0%

The results from the 800 m.l. distillations more nearly represent the actual yields of the various fractions which would be obtained in large scale work.

The results given above and those previously quoted under the individual runs indicate that there is no great difference between the New South Wales and Tasmanite shale oils as regards volatility and that in the case of laboratory produced oils about 40% of the original crude distils off below 300°C. and that the crude straight run petrol amounts to 10 to 13%, depending on the cutting temperature and the efficiency of the original condensation. This percentage of crude petrol does not include the scrubber spirit which amounts to some gallons per ton.

SPECIFIC GRAVITY, SATURATION AND SULPHUR CONTENT OF CRUDE OILS AND DISTILLATES.

The specific gravity of New South Wales shale oil is lower than that of Tasmanite oil and in round figures .05 unit different.

The specific gravity of crude oils distilled from different samples of Tasmanite under approximately the same conditions used for the distillation work on the New South Wales shales varies from 0.908 to 0.926 with about 0.913 as an average figure. The specific gravities of the New South Wales oils were more constant, ranging from 0.865 to 0.874. These differences are naturally reflected in the specific gravities of the fractions and comparison of fractions of similar mid-point show notable differences, e.g. New South Wales fractions 170°C.-230°C. have a specific gravity of 0.795 average, while the 175°C.-225°C. fraction from Tasmanite oil runs 0.849.

The specific gravities and saturations of many fractions are given in the next section.

The saturation or percentage soluble in 3 volumes of 1.84 specific gravity sulphuric acid has been determined consistently all through, but those figures which were obtained in the first work on New South Wales shale oils in 1930 are too high, as the acid was found later to be somewhat weak and the figures though comparative are misleading. Later work in 1933 showed the laboratory produced Newnes and Capertee crudes to be 36% saturated, using acid of 97.5% strength, while the oils produced in the 100 lb. retort from the same shales ran 42% and 40% respectively. The Newnes commercially produced oil ran lower - 32% - though this is explainable by the almost complete absence of the petrol fraction.

Sulphur content of crude oils and distillates. As the sulphur magnitudes in the case of New South Wales oils are much less than in the case of Tasmanite oils, not so much attention was devoted to the sulphur position, especially when it was found that the petrols could be refined to quite small sulphur contents by the use of allowable amounts of reagents.

The sulphur contents of the various crude oils determined by the sodium peroxide bomb method are given below.

Laboratory produced oils.

Hartley Vale shale	0.29%
Capertee No. 1 shale	0.32%
do. v.p. cracked at 560°C.	0.48%
do. v.p. cracked at 650°C.	0.63%
Capertee No. 2 shale	0.36%
Newnes shale	0.33%
Capertee shale No.2 - 100 lb. retort	0.54%
Newnes shale - 100 lb. retort	0.46%
Newnes shale - Commercial retorts	0.56%

As far as crude fractions are concerned, very few sulphur determinations were made on these. In the case of Hartley Vale and Capertee fractions distilling below 150°C. the sodium peroxide method gave 0.05% S. in each case, but it is not clear from the notes made at the time whether these fractions were soda washed to remove hydrogen sulphide. The 150°C.-300°C. fraction from the Hartley Vale and Capertee oils ran 0.22% S. and 0.32% S respectively. The sulphur content of the corresponding fraction of Tasmanite oil is 2.8%, so that the Capertee oil fractions contain little more than one-tenth of the sulphur content of the Tasmanite oil fractions. In the case of the petrol fraction the disparity is still greater.

The setting point of the crude oil varies with the amount of vapour phase cracking and the completeness of condensation of the lower boiling fractions with the remainder of the oil. In the laboratory distillations in which the amount of uncondensed spirit is at a minimum, the crude oil has a setting point around 12°C. Both the Newnes and Capertee crude oils are solid at 10°C., though they will work to a paste with a stirring rod. The apparently solid condition is caused by the interlacing of wax crystals and this occurs to a greater degree when the oil is stationary. When the oil is moving a somewhat lower temperature is necessary for freezing. The Newnes oil becomes noticeably liquid at 12°C., while at this temperature the Capertee is not appreciably melted, but is liquefied fairly completely at 15°C. Even the highest boiling wax fractions are completely melted at 25°C., with the exception of oil boiling above 400°C. which at 25°C. still shows a sprinkling of feathery wax crystals.

COMPOSITION OF NEW SOUTH WALES SHALE OIL DISTILLATES.

Work under this heading has been principally confined to oils distilled from shale from the Newnes and Capertee areas. It is convenient for the sake of uniformity to retain the oil numbers previously used, viz:

Oil No. 1 - distilled from Capertee No. 2 sample in 2 lb. retort.
Oil No. 2 - distilled from Capertee No. 2 sample in 100 lb. retort.
Oil No. 3 - distilled from Newnes shale in 2 lb. retort.
Oil No. 4 - distilled from Newnes shale in 100 lb. retort.
Oil No. 5 - distilled from Newnes shale in the commercial retorts at Newnes in New South Wales.

None of the oils include the scrubber spirit, though condensation has been much more complete in the case of oils 1, 2, 3 and 4 compared with 5.

The specific gravities at 15°C., saturations, and sulphur contents of these oils are as follows:-

Oil	1	2	3	4	5
Specific gravity	0.865	0.863	0.874	0.869	0.894
Saturation	36%	40%	36%	42%	32%
Sulphur content	0.36%	0.54%	0.33%	0.46%	0.56%

By examining these figures and referring to the distillation analyses given in that section it will be seen that there is close similarity between oils 1 and 2 and again between 3 and 4, so that as 1 and 3 were only available in small quantity, work was confined to 2, 4, and 5 as regards ascertaining hydrocarbon composition etc.

In order to determine the hydrocarbon composition of the various fractions the method using sulphuric acid of varying concentration was used. This method is open to criticism in certain particulars, especially as regards its application to cracked spirit and similar oils. As shale/fractions are similar in some respects to cracked products the use of such a method is not free from objection. Viewed from a different angle, however, the method gives direct information as regards sulphuric acid refining and thus is perhaps more useful than some of the methods more recently proposed but against which weighty criticism has also been launched.

/oil

The scheme of treatment adopted was as follows:

Treatment.	Relative volume of reagent used for the various fractions.				
	-170°C.	170°C.-230°C.	230°C.-300°C.	300°C-350°C.	+ 350°C.
For Acid Oils					
10% Sodium hydroxide	1.0	1.5	2.0	2.5	3.0
For Basic Oils					
10% Sulphuric acid	1.0	1.5	2.0	2.5	3.0
For Olefines					
83% Sulphuric acid	2.0	2.0	2.0	2.5	3.0
For Aromatics					
Washed with 97.5%					
Sulphuric acid to	2.0	2.0	2.0	2.0	2.0
constant oil volume	1.0	1.0	1.0	1.5	1.5
	0.5	0.5	0.5	0.5	0.5

The treated oil was then washed with 10% sodium hydroxide solution and dried over calcium chloride. The aniline points of the paraffin residues were determined as well as the melting ranges of the paraffin residues in the higher boiling ranges. The aniline used was pure, freshly redistilled and dried with potassium carbonate.

In carrying out the above mentioned acid and alkali treatments, only one stage a day was carried out, i.e., after thorough agitation with the reagent, settlement for nearly 24 hours was allowed, assisted by warmth to lower viscosity in the case of the higher boiling fractions. In this way it was possible to work on the higher fractions as well as the lower boiling ones.

The petrol fractions are subject to a small evaporation loss, which is counted in with the phenols, but this loss has been kept at a minimum by using separatory funnels of just sufficient volume. The same funnel and the same graduate was used for each fraction till treatment was finished, so that no cumulative error crept in, and the final draining of the funnel was assisted by heat and given ample time. Carbon tetrachloride washing of the drained funnels showed that the amount of oil left as a film on the funnel was below 0.2% of the oil originally taken.

The separation of acid and basic tars etc. from the oil is very difficult in the fractions boiling over 300°C., so that an occasional anomalous result appears, such as the basic content of oil No. 4 300°C.-350°C. fraction, which possibly is too high. In the case of the two lowest boiling fractions, the oil volumes could be read to 0.2% of the original volume with ease.

The Capertee scrubber spirit obtained in the laboratory distillation was given 83% acid as a first treatment to avoid the evaporation losses inevitable in handling this spirit. Its acid and basic content would be under 1% each, so that these are not shown. Likewise the spirit boiled out of the aniline mixture below the aniline point, so that this point corresponds more to the heavier portion of the spirit.

Aromatic removal was effected by 97.5% acid because no stronger acid could be obtained here. The oil volumes were read after each of the

three 97.5% acid treatments and the last treatment caused no decrease in volume in all cases. It is possible that acid 1% or so stronger would have removed a little more oil, but the point is by no means certain. Certain benzene derivatives, such as hexa-alkyl benzenes, are stated to be unattacked by sulphuric acid of 98% strength so that, with this possible exception, the final residue should be naphthenes and paraffins.

The percentages of final residues are shown below, together with the aniline points, the aniline points for pure paraffins of the same boiling range, the percentage of naphthenes present on the basis of 0.2°C. depression of the aniline point for each 1% of naphthene present and the melting ranges of the higher fractions.

The percentage of naphthenes present in the final residue has been calculated on the basis that each 1% lowers the aniline point of the pure paraffin 0.2°C. The unit depression figure is variously given as 0.3 and 0.4°, but the more recent information available indicates 0.2°C. as the correct figure. If the larger figures are taken the percentage of naphthenes is reduced in the ratios 2/3 and 1/2 respectively.

Aniline Point Data.

No. 2 Capertee.

	Residue %	A.P. °C.	A.P. Pure Paraffin.	% Naphthenes.	Melting Range °C.
- 170°C.	63.6	72.5°C.	73°C.	2.5	-
170°C. - 230°C.	62.8	75.2	82	34	-
230°C. - 300°C.	52.5	85.5	95	48	-
300°C. - 350°C.	42.5	98.0	107	45	12-20
+ 350°C.	31.5	106.0	118	60	25-37
350°C.- 375°C.	-	-	-	-	-
+ 375°C.	-	-	-	-	-
Scrubber spirit from Capertee shale laboratory distilled	67.0	73.0	73.0	0	-

No. 4 Newnes.

- 170°C.	63.2	72	73	5	-
170°C. - 230°C.	~~59.6~~ ~~62.8~~	~~74.5~~ ~~75.2~~	82	34	-
230°C.- 300°C.	51.5	85.5	95	48	-
300°C.- 350°C.	40.5	99.0	107	40	12-20
+ 350°C.	31.5	106.5	118	58	25-36
350°C. - 375°C.	-	-	-	-	-
+ 375°C.	-	-	-	-	-

Aniline Point Data continued.

No. 5 Newnes Commercial.

	Residue %	A.P. oC.	A.P. Pure Paraffin.	% Naphthenes.	Melting Range oC.
- 170°C.	62.5	73.0	75.2	11	-
170°C. - 230°C.	55.8	77.5	82	22	-
230°C. - 300°C.	46.0	86.2	95	44	-
300°C. - 350°C.	37.5	98.0	107	45	12-20
+ 350°C.	-	-	-	-	-
350°C. - 375°C.	31.7	105.2	115	49	20-30
+ 375°C.	25.5	106.0	120	70	23-37.

The composition of the fractions of the Capertee and Newnes oil distilled in Melbourne and of the Newnes Commercial oil may now be given as shown in the following tabulated results of the experimental work. Specific gravities at 15°C. and saturation percentages determined by mixing with 3 volumes of 97.5% sulphuric acid and centrifuging after reaction are given for each fraction for comparative purposes. Included in the table is shown Capertee scrubber spirit distilled off from the absorber oil. The actual recovery was 4.0 gallons per ton out of the 4.75 indicated by the increase in volume of the scrubbing oil. The volatility of the spirit would account for this loss.

PERCENTAGE COMPOSITION OF FRACTIONS.

No. 2 - Capertee oil - distilled in Melbourne, 100 lb. Retort.

Fraction.	Sp. Gr.	Saturation.	Acid oils.	Basic oils.	Olefines.	Aromatics.	Naphthenes.	Paraffins.
- 170°C.	.732	68%	1.4	1.6	9.5	23.9	1.5	62.1
170°C.-230°C.	.792	66	2.0	1.2	11.8	22.2	21.4	41.4
230°C.-300°C.	.843	58	4.0	2.5	11.0	30.0	25.2	27.3
300°C.-350°C.	.876	52	3.5	2.5	15.0	36.5	19.1	23.4
+ 350°C.	.891	40	5.0	2.5	20.0	41.0	18.9	12.6
Scrubber spirit Capertee.					21.5	11.5	0.0	67.0

No. 4 - Newnes Oil - distilled in Melbourne, 100 lb. Retort.

Fraction.	Sp. Gr.	Saturation.	Acid oils.	Basic oils.	Olefines.	Aromatics.	Naphthenes.	Paraffins.
- 170°C.	.739	68%	1.4	1.6	9.8	24.0	3.2	60.0
170°C.-230°C.	.795	64	2.6	1.6	11.8	24.4	22.6	37.0
230°C.-300°C.	.850	56	3.2	2.8	11.5	31.0	24.7	26.8
300°C.-350°C.	.884	48	3.5	4.0	18.5	33.5	16.2	24.3
+ 350°C.	.900	38.	5.5	2.0	25.5	35.3	18.3	13.2

No. 5 - Newnes Oil - distilled in Newnes Commercial Retorts.

Fraction.	Sp. Gr.	Saturation.	Acid oils.	Basic oils.	Olefines.	Aromatics.	Naphthenes.	Paraffins.
- 170°C.	.768	64%	2.5	1.0	8.0	26.0	6.9	55.6
170°C.-230°C.	.798	60	3.5	1.9	9.0	29.8	12.3	43.5
230°C.-300°C.	.846	52	4.5	3.0	9.0	37.5	20.4	25.6
300°C.-350°C.	.882	44	5.0	2.5	17.5	37.5	16.8	20.7
350°C.-375°C.	.895	40	4.5	3.5	22.0	38.3	15.5	16.2
+ 375°C.	.904	36	6.0	4.0	22.5	42.0	17.8	7.7

Reviewing the results it may be said that the Newnes and Capertee oils distilled in the 100 lb. retort are closely similar fraction for fraction. The Newnes oil is higher in gravity and a little less saturated, corresponding to a somewhat lower paraffin content. The general hydrocarbon composition is much the same and the phenols and basic oils about the same. The naphthene content of the petrol fractions is very low and cycloparaffins appear to be absent from the scrubber spirit. The naphthene content of the Newnes commercial - 170°C. fraction is higher as it has a much higher average boiling point than the petrol fraction proper. The naphthene content of the higher boiling fractions is considerable and is greater than the true paraffin content in the heavier lubricating oil fractions.

The Newnes commercially produced oil on the other hand is less saturated than its counterpart produced in the smaller retort. The content of acid and basic oils averages about 30% higher and on the whole it is richer in aromatics at the expense of the paraffins, especially in the higher boiling ranges. This would indicate increased vapour phase cracking having taken place in the commercial retort compared with the small retort.

Comparison of New South Wales Crude shale oil distillates with those from Tasmanite shale oil.

The Capertee and Newnes oils distilled in the 100 lb. retort are comparable with the Tasmanite laboratory produced oils, while the Newnes commercially produced oil is more or less comparable with the commercial Tasmanite oil. The cutting temperatures were not the same in all cases but the comparison is not affected thereby if the mid-points of the various fractions are taken into account.

Laboratory produced oils.

Comparing then the fractions from oils 2 and 4 up to 300°C. with the corresponding fractions from laboratory produced Tasmanite oil, it is seen that the oxygenated acidid oils in Tasmanite distillates are twice as great as in the Capertee or Newnes oils, while the basic oils are also approximately twice as great as in the New South Wales oils. The olefine content of the Tasmanite distillates is on the average from 2.5 to nearly 3 times that of the New South Wales oils. The aromatic content is not greatly different but is lower on the average in the New South Wales oils. It must be borne in mind, however, that the thiophene homologue content of the Tasmanite

distillates is considerable and in non-sulphurous cyclic compounds the New South Wales oils are therefore richer. With the exception of the petrol fraction, the New South Wales oils are richer in naphthenes being approximately twice as rich as Tasmanite distillates in these compounds. The true paraffin content of the New South Wales oils is nearly double in the petrol range and in the higher kerogene range is several times that of Tasmanite oil.

In the New South Wales oils true paraffins are found in appreciable percentages right through to the highest boiling distillates, but they practically disappear from the Tasmanite distillates at about 330°C. boiling point.

Commercially produced oils.

It is difficult to compare the Newnes commercially produced oil with the Tasmanite commercial oil with any approach to exactness. In each case there would be more vapour phase cracking taking place in retorting than occurs in a laboratory sized retort, and the Tasmanite oil was produced under somewhat adverse conditions as regards vapour phase cracking.

The acid and basic contents of the Tasmanite oil fractions are each approximately 1.5 times those of the Newnes oils. The olefine contents of the Tasmanite oil fractions are likewise approximately 2.5 times those of the Newnes oil, while the aromatic contents are about the same. With the exception of the highest boiling distillate, the Newnes fractions contain less naphthenes than paraffins, whereas the reverse is true with Tasmanite oil fractions. The average naphthene content of the Tasmanite oil fractions is decidedly greater than in the case of the Newnes oil, while the true paraffin content of the Newnes oil fractions is fully double that of the Tasmanite oil fractions.

The naphthene content of the -170°C. fraction of Newnes commercial oil is appreciable, but the mid-point of this fraction was about 160°C. so that the petrol fraction proper would probably show a very small naphthene percentage.

Newnes petrol is thus almost free from naphthenes, especially if scrubber spirit formed an appreciable part, whereas in M.O.E.L. refined petrol from Tasmanite oil the naphthene-paraffin ratio was 1.32 to 1.

Reviewing the compositions of distillates from New South Wales and Tasmanite shale oils in a general way, it may be said that the higher acid, basic, and olefine content of the Tasmanite distillates compared with the New South Wales oils must result in much heavier refining losses and reagent costs. The commercial production of petrol from the New South Wales shale oil is thus much more likely to be successful than in the case of Tasmanite oil, as refining costs and losses would be much reduced and in refining the spirit gum stable and sufficiently good in colour the sulphur is brought within accepted limits.

REFINING OF NEW SOUTH WALES SHALE OIL DISTILLATES.

As a definite programme of investigation of the New South Wales shale position has been drawn up and proceeded with by the Commonwealth Government, any extensive work on refining was not undertaken. During 1930, however, some preliminary work was done on the limited quantities of distillates then available and it may be of interest to give the details.

The samples of oil distilled and refined were from Run 101, Hartley Vale, Run 103, Capertee No. 1, and Run 104, Capertee No. 1 with vapour phase cracking at 560°C. The increase in the yields of petrol and kerosenes with vapour phase cracking is instructive.

As the amount of crude petrol available was only 50 m.l., and of the kerosene fraction 100 m.l., the losses in so many treatments are bound to be much larger than would be experienced in larger scale work. However, the greatest care was exercised to keep losses down and as the actual loss of dl in treating the petrol fraction - excluding the distillation residue passed on to the kerosene treatment - averages about 10% it is seen that refining losses even on such a small scale are relatively low. With larger quantities better results on the petrol fraction would be secured, but it is expected that the results on kerosene would be about the same, since evaporation loss is small and the quantity available was larger for the kerosene fraction.

The details of the refining procedure are given in the following tabular form. Acid percentages are by volume. A cutting temperature of 175°C. was used for petrol and 300°C. for kerosenes. The quantities given are pereentages of the original condensed crude oil, which does not include scrubber spirit. The actual refined petrol yields given in the tables would be subject to a substantial increase if the retort gas was fairly completely scrubbed and this spirit added to the distilled petrol.

HARTLEY VALE OIL FROM RUN 101.

The crude oil was distilled, yielding as percentages of the original:-

Crude Petrol -	175°C.	12.6% by volume.
Crude kerosenes	175°C.-300°C.	25.7% " "
Residuum & loss	+ 300°C.	61.7%

Treatment of Crude Petrol 12.6%.

10% soda wash
1% by volume of 95% acid.
1% do.
2½% soda wash.
Redistilled to 175°C.

Products.

Refined Petrol -	175°C.	10.1%	
Residue	+ 175°C.	1.0%	added to kerosenes.

Hartley Vale Oil from Run 101 continued.

Treatment of crude kerosenes 26.7%.

10% soda wash
1% by volume of 95% acid.
1% " " " " "
1% " " " " "
2½% soda wash.
Redistilled into fractions

- 200°C.	6.7%
200°C.-225°C.	4.7
225°C.-250°C.	4.85
250°C.-300°C.	5.4
+ 300 residue	2.0

Combined fractions for retreatment as follows:

1% by volume of 95% acid.
1% " " " " "
2½% soda washed.
Redistilled into fractions

- 200°C.	6.4
200°C.-225°C.	4.1
225°C.-250°C.	4.1
250°C.-300°C.	5.2
+ 300°C. Residue	2.6%

Refined Products - Percentages of original crude.

	1st. Treatment.	2nd. Treatment.
Petrol - 175°C.	10.1%	10.1%
Power Kerosene 175°C.-225°C.	11.4%	10.5%
Heavy Kerosenes 225°C.-300°C.	10.25%	9.3%
Residue	2.0%	2.6%
Total recovered	33.75%	32.5%
Oil treated	38.3%	38.3%
Lost in refining	4.55%	5.8%

CAPERTEE OIL FROM RUN 103.

The crude oil was distilled, yielding as percentages of the original

Crude Petrol	- 175°C.	13.4%
Crude Kerosenes	175°C.-300°C.	28.0%
Residuum + loss	+ 300°C.	58.6%

Capertee Oil from Run 103 continued.

Treatment of Crude Petrol.

10% soda wash.
1% by volume of 95% acid.
1% " " " " "
2½% soda wash.
Redistilled to 175°C.

Products.

Refined petrol	- 175°C.	11.0%	
Residue	+ 175°C.	1.0%	added to kerosenes.

Treatment of Crude Kerosenes 29.0%.

10% soda wash.
1% by volume of 95% acid.
1% " " " " "
1% " " " " "
2½% soda wash.
Redistilled into fractions

- 225°C.	11.4%
225°C.-300°C.	12.0
+ 300°C. residue	2.9

Combined fractions for retreatment as follows:-

1% by volume of 95% acid.
1% " " " " "
2½% soda washed.
Redistilled into fractions

- 200°C.	5.6%
200°C.-225°C.	5.3%
225°C.-250°C.	4.1%
250°C.-300°C.	6.75%
+ 300°C. residue	3.3%

Refined Products - Percentages of original crude.

		1st. Treatment.	2nd. Treatment.
Petrol	- 175°C.	11.0	11.0
Power Kerosene	175°C.-225°C.	11.4	10.9
Heavy Kerosenes	225°C.-300°C.	12.0	10.85
Residue		2.9	3.3
Total recovered		37.3	36.05
Oil treated		41.4	41.4
Lost in refining		4.1	5.35

VAPOUR PHASE CRACKED CAPERTEE OIL FROM RUN 104.

The crude oil was distilled, yielding as percentages of the original

Crude petrol	- 175°C.	19.3%
Crude kerosenes	175°C.-300°C.	33.0%
Residuum + loss	+ 300°C.	47.7%.

Treatment of crude petrol.

10% soda wash.
1% by volume of 95% acid.
1% " " " " "
2½% soda wash.
Redistilled to 175°C.

Products.

Refined petrol	- 175°C.	15.5%	
Residue	+ 175°C.	2.2%	added to kerosenes.

Treatment of crude kerosenes 35.2%.

10% soda wash.
2% by volume of 95% acid.
2% " " " " "
1% " " " " "
2½% soda wash.
Redistilled into fractions as follows

- 250°C.	20.5%
250°C.-300°C.	7.5%
+ 300°C. residue	3.0%

Refined Products - percentages of original crude.

Petrol	- 175°C.	15.5%
Kerosene	175°C.-250°C.	20.5%
Heavy kerosene	250°C.-300°C.	7.5%
Residue		3.0%
Total recovered		46.5%
Oil treated		52.3%
Lost in refining		5.8%.

The general characteristics of the refined oils were as follows:

Fraction.		Colour.	Sp. Gr.	Saturation.	% S.
Hartley Vale	- 175°C.	White	0.736	86%	0.04%
	175°C.-250°C.	light straw	0.797	82%	0.17
	250°C.-300°C.	light yellow	0.841	78%	0.45
Capertee	- 175°C.	white	0.731	86%	0.06
	175°C.-250°C.	lighter straw	0.796	92%	0.06
	250°C.-300°C.	lighter yellow	0.841	84%	0.33
Cracked Capertee	- 175°C.	very white	0.731	86%	0.06
	175°C.-250°C.	darker straw	0.801	90%	0.17
	250°C.-300°C.	darker yellow	0.851	82%	0.55

The Hartley Vale and Capertee petrols were very pleasant smelling, while the cracked Capertee petrol was less pleasant but as good as most commercial petrols are now.

All the petrols proved gum stable and of permanently good smell when kept in white bottles exposed to light for many months, conditions which would have seriously altered most commercial petrols. In general less acid could be used on a larger scale and the substitution of activated bauxite treatment for the later portions of acid would probably be an improvement in refining technique. The work on Tasmanite oils has indicated oleum to be more effective than 93-95% acid for refining shale oil distillates and, as the latter was used in this work, the use of oleum might show an improvement in sulphur content in the kerosene fraction.

The saturation percentages are perhaps a little low as the acid used was 95%, but they are comparative.

The hypochlorite process was also tried but effected little sulphur removal, if any, from the kerosene fraction. The equivalent chlorine consumption was 0.08 lbs. per gallon for Hartley Vale oil and 0.065 lbs. per gallon for Capertee oil up to the end of rapid oxidation. The oil was distinctly yellowed by the treatment and was noticeably chlorinated in spite of the use of an alkaline solution. As with Tasmanite distillates, the hypochlorite process appears unsuitable for the refining of New South Wales shale oils, owing mainly to the large olefine content.

WAX CONTENT OF NEW SOUTH WALES SHALE OILS.

The New South Wales shale oils have, compared with Tasmanite shale oil, a large wax content. However, the sulphuric acid insoluble portion of the oil does not consist entirely of straight chain paraffins, but an appreciable proportion of cyclo paraffins or naphthenes is also present. The apparent waxes are thus somewhat different in character and lower in melting point than would be expected from their boiling point. Waxes crystallise out from the crude oil at temperatures below 20°C. depending on the treatment that the shale has undergone. In the case of residuum left at 300°C. the waxes naturally crystallise out at higher temperatures.

In order to study the paraffin content of the oil, residuum from Capertee oil produced in the 100 lb. retort was distilled with 10°C. cuts, using a thermocouple for determining the vapour temperature. The residuum had been left from distillations in which a thermometer had been used thus accounting for the smallness of the - 340°C. fraction. The amount of residuum used was 731 grams of specific gravity 0.913, representing 59.3% by volume of the crude oil. The percentages by weight of the fractions insoluble in 97% sulphuric acid were then determined.

The results are shown in the following table where the temperatures given are vapour temperatures, specific gravities are at 15°C. and for the solidified state in the heavier fractions, and percentages are by weight.

Fraction.	Grams.	% of whole.	Sp. Gr.	Paraffin Residue %.	Melting Range Solid-liquid.
Original	731	100	.913		
- 340°C.	56.0	7.65	.866	43.0	below 18°C.
340°C.-350°C.	41.2	5.64	.873	39.4	below 18°C.
350°C.-360°C.	42.8	5.85	.879	38.7	below 25°C.
360°C.-370°C.	72.6	9.94	.883	38.4	18°C.-26°C.
370°C.-380°C.	71.5	9.73	.889	32.6	25°C.-29°C.
380°C.-390°C.	105.9	14.50	.895	31.4	25°C.-34°C.
390°C.-400°C.	194.2	26.60	.901	28.8	26°C.-37°C.
400°C.-403°C.	79.5	10.88	.912	21.7	26°C.-42°C.
Residue	45.0	6.16	-		
Loss-gases etc.	22.3	3.05	-		

There was a small delay in changing the receiver at 370°C., making the previous fraction too large and the following one too small. The use of a thermocouple instead of a thermometer has also had the effect of reducing the amount of the -340°C. fraction.

The melting ranges of the paraffinic residues from sulphuric acid treatment are a little difficult to determine as they consist of naphthenes and true waxes. What is apparently a solid will work to a paste on stirring, owing to the presence of some liquid oil between the wax crystals. This oil would represent some of the naphthene content and the presence of a considerable proportion of naphthene hydrocarbons dissolves the wax below its true melting point. The upper limit of the melting range is therefore

below the melting point of the wax which is last to dissolve or melt.

The usual method of separation of the waxes from the wax fractions is to filter off the crude wax and sweat it, which is really a liquation process. The paraffin hydrocarbons in the fractions distilling below 350°C. are too low melting to be called waxes commercially. Over 50% of the residuum corresponding to 30% of the crude oil distils over above 380°C. and this is the principal wax fraction. From 350°C.-380°C. a softer wax fraction is collected representing about 15% of the original crude oil.

One simple sweating experiment made on the Capertee and Newnes fractions + 350°C. may be quoted. These fractions were quite liquid at 25°C. and fairly firmly solid at 12°C. On filtering at 18°C. after standing for some time at the same temperature they yielded crude oily wax as follows:-

Capertee: 29.5% of original fraction by weight.
Newnes: 28.9% " " " " "

These crude oily waxes contained the other types of hydrocarbons in considerable amount as on sulphuric acid treatment the yields of wax were

Capertee: 9.30% of original fraction, melting range 30°C.-45°C.
Newnes: 7.70% " " " " " 30°C.-36°C.

It will be noticed from the composition tables given earlier that above 350°C., especially in the commercially produced oil, naphthenes are more abundant than true paraffins, so that the waxes from the hard wax fractions are rather disappointing in melting point, if hard waxes are being sought.

It is possible by sweating or liquation methods to obtain waxes of higher melting point, but the yield becomes smaller as the melting point is raised; e.g., by filtering a 300°C. Capertee residuum at 20°C. followed by sweating on filter paper for some considerable time at 25°C. a residue was obtained which on purification gave a wax of 52°-55°C. melting range. The quantity was 0.08 lbs./gallon of crude oil, or, say, 8 lbs. per ton of shale. It is also approximately 1% by weight of the crude oil. This wax would represent very nearly the highest melting waxes extractable in any appreciable quantity. In order to thoroughly examine the wax position, much work would be needed especially as regards separation of naphthenes from the true paraffins.

For the production of wax from crude residuum or bottoms left after the taking off of the kerosenes and light lubricating oils, filtration at temperatures lower than 25°C. is necessary and the lower the temperature the greater the amount of crude wax separated and the lower the average melting point of the purified wax. From the meagre amount of work done on the waxes, it would appear that unless naphthenes are removed the amount of hard wax of melting point over 50°C. is rather small compared with the total paraffin content of the oil. With each few degrees lowering of the melting point the amount of recoverable wax increases largely.

SHORT GENERAL SUMMARY OF NEW SOUTH WALES SHALE PROSPECTS AS COMPARED WITH THOSE OF TASMANITE SHALE.

In the first place, the available tonnage of shale in New South Wales is much greater than in Tasmania and the probability of the discovery of further workable areas of shale in Tasmania is small. It is true that many of the shale seams in New South Wales are thin, but they are also comparatively rich. The Tasmanite seam is a thicker one, but contains a more or less barren middle band, which is unprofitable to treat. Mining costs on New So uth Wales shale would, according to qualified opinion, be nearly double per ton of shale compared with Tasmanite, but on a volume basis approximately the same. As the oil content of the New South Wales shale averages fully three times that of average top and bottom seam Tasmanite, mining costs per ton of oil are decidedly less for New South Wales shale. Haulage and handling costs are also correspondingly lower per ton of oil.

Retorting of Tasmanite is undoubtedly an easier proposition than retorting the New South Wales shale, but the latter can be done satisfactorily. The retort residue from New South Wales shale is sufficiently high in carbon to be a useful fuel for producer gas, or it can be gasified in suitable retorts for increasing the gas yield for heating purposes. The amount of retort residue to be handled and dumped is thus many times smaller per ton of oil produced, than in the case of Tasmanite shale.

As far as the oil is concerned, the New South Wales oil is by far the most attractive commercially. With the possible exception of the property of solidifying at low temperatures making it impossible to pump the oil any distance in cold weather without heating, the New South Wales oil is superior in every way. Its sulphur content is only 10% to 15% of that of Tasmanite oil and its nitrogen content either lower or less obnoxious. The smell of Tasmanite crude oil is largely determined by its sulphur, nitrogen, and oxygen content and for bakers ovens etc. the odour of the crude oil might possibly prohibit its use, but the smell of the New South Wales oil is much less noticeable. It will be gathered from the comparison of the oils that the higher acidic, basic, and olefine content of the Tasmanite oil fractions must entail higher refining losses and costs and in addition, owing to the thiophenic sulphur content of the Tasmanite distillates, they can not be made into standard products by ordinary refining methods. Further, the sulphur content of New South Wales shale oil distillates increases progressively with the boiling point, so that very little sulphur removal is necessary from the petrol fraction and not a great deal more from the power kerosene fraction. With Tasmanite oil distillates the maximum sulphur content occurs in the power kerosene fraction, or at the end of the petrol range, and these products cannot with reasonable expenditure of reagents and loss of oil in refining be made to conform to present day accepted standards.

Owing to the more saturated nature of the New South Wales oils they would probably be more suitable for use in liquid phase cracking plant, and this point is of paramount importance in connection with the motor fuel position.

As a potential source of lubricants the New South Wales oil with its very considerable naphthene and paraffin content is very much better than Tasmanite oil, and the possibility of the production of waxes from the New South Wales oils gives an additional outlet for some of the production.

In general it would appear that the preference being given to the exploitation of New South Wales shale is fully justified by the results of the writer's investigation of the two shales, and the commercial prospects of the Latrobe field are very discouraging compared with those of the Capertee area.

CONCLUSION.

It is hoped that the results of this investigation of the Tasmanian and New South Wales oil shales and derived oils, as reported in the foregoing pages, will prove useful. Primarily the investigation was intended to be confined to the Tasmanite shale and, therefore, with it the greater part of this work is concerned, but the smaller portion dealing with the New South Wales shales is by no means the least important, serving as it does to provide data for a valuable comparison.

The ground covered has been much greater than at first intended, and the widening of the field of enquiry has resulted in some of the work being more superficial than the writer would desire. On reviewing the whole of the matter dealt with, and considering that it is the work of one person interrupted on numerous occasions by diverse causes, it will probably be conceded that a fairly comprehensive programme has been covered.

The results of the investigation are therefore presented with the hope that they will prove useful in suggesting starting points for future work and in enabling any such work to be embarked upon having a general background of knowledge already to hand which in the case of Tasmanite shale did not previously exist.